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A

HANDBOOK

OF

CHEMICAL TECHNOLOGY

BY RUDOLF WAGNER, PH. D.,

PROFESSOR OF CHEMICAL TECHNOLOGY AT THE UNIVERSITY OF WURTZBURG.

Translated and Edited from the Eighth German Edition,
with Extensive Additions,

BY WILLIAM CROOKES, F. R. S.

WITH 886 ILLUSTRATIONS.

NEW YORK:
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1877.

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1877

TRANSLATOR'S PREFACE.

THE several Editions of Professor RUDOLF WAGNER'S "Handbuch der Chemischen Technologie" have succeeded each other so rapidly that no apology is needed in offering a translation to the public.

There is little to be said as to the arrangement. Improvements in Technological processes that have appeared since the publication of the Eighth German Edition have been added during translation. Only when necessary have Foreign weights and measures been stated in English equivalents; where the point has been one of comparison, the weights have been left unaltered. The Metrical System has in some cases been of great service in avoiding the repetition of tiresome distinctions between English and Prussian grain weights, English and Bavarian foot measure, &c. The formulæ have been subjected to careful revision, and are molecular throughout. Indeed, every care has been taken to merit the confidence of the manufacturer and of the student.

Under the head of Metallurgical Chemistry, the latest methods of preparing Iron, Cobalt, Nickel, Copper, Copper Salts, Lead and Tin and their Salts, Bismuth, Zinc, Zinc Salts, Cadmium, Antimony, Arsenic, Mercury, Platinum, Silver, Gold, Manganates, Aluminum, and Magnesium, are described. The various applications of the Voltaic Current to Electro-Metallurgy follow under this division. The Preparation of Potash and Soda Salts, the Manufacture of Sulphuric Acid, and the Recovery of Sulphur from Soda-waste, of course occupy prominent places in the consideration of chemical manufactures. It is difficult to over-estimate the mercantile value of Mond's process, as well as the many new and important applications of Bisulphide of Carbon. The Manufacture of Soap will be found to include much detail. The Technology of Glass, Stoneware, Limes, and Mortars, will present much of interest to the builder and engineer. The Technology of Vegetable Fibres has been considered to include the preparation of Flax, Hemp, Cotton, as well as Paper Making; while the applications of Vegetable Products will be found to include Sugar-boiling, Wine and Beer Brewing, the Distillation of Spirits, the Baking of Bread, the Preparation of Vinegar, the Preservation of Wood, &c.

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TRANSLATOR'S PREFACE.

Dr. Wagner gives much information in reference to the production of Potash from Sugar residues. The use of Baryta Salts is also fully described, as well as the Preparation of Sugar from Beet-roots. Tanning, the Preservation of Meat, Milk, &c., the Preparation of Phosphorus and Animal Charcoal, are considered as belonging to the Technology of Animal Products. The Preparation of the Materials for Dyeing has necessarily required much space; while the final sections of the book have been devoted to the Technology of Heating and Illumination.

We cannot let this work pass out of our hands without expressing the hope that, at no distant date, Chairs of Technology will be founded in all our Universities, and that the subject will be included in the curriculum of every large school.

London, *May*, 1872.

AUTHOR'S PREFACE TO THE EIGHTH EDITION

THE Eighth Edition of my "Chemischen Technologie" having followed the Seventh within two years, but few words of introduction are necessary.

The arrangement of the subject-matter in former Editions has essentially been left unaltered, with the exceptions that I have brought the consideration of the materials and products of Chemical Industry, and the Technology of Glass and of Stoneware, in former Editions arranged as one section, under distinct headings The various processes of Chemical Manufacture have had much detail added. The descriptions of the Technological Preparation of Alkali and Ammoniacal Salts, as well as of the Tar-colours, have in consequence of the extended application of these products, been much enlarged. The Chemical formulæ are molecular. throughout.

Of the present Edition translations will be made into English by Mr. WILLIAM CROOKES, of London, and into French by Professor L. GAUTIER, of Melle, Deux-Sèvres. A translation into Dutch of part of the Seventh Edition that has recently appeared has been made without my permission or that of my publishers.

The First Edition of this work, written whilst I held the position of Private Tutor in Chemistry to the Philosophical Faculty to the High-School of Leipsic, appeared in September, 1850. The Second in May, 1853, and the Third Edition in July, 1856, were presented to the public during my Professorship of Technological Chemistry in the Imperial Industrial Schools of Nuremburg. The later Editions appeared—

The Fourth in May, 1859.
,, Fifth in May, 1862,
,, Sixth in October, 1865,
,, Seventh in March, 1868,

during intervals in my official duties in Wurtzburg; and in these I have been much assisted by the contributions and suggestions of many friends, to whom I now tender my sincere thanks.

DR. RUDOLF WAGNER.

UNIVERSITY OF WURTZBURG,
December 10th, 1870.

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INTRODUCTION.

MAN's labour, considered from an economical point of view, is of a threefold kind, being either productive, improving, or converting. We distinguish likewise between the productions obtained from the soil taken in its widest sense, and between commerce and manufacturing industry.

The department of labour, the object of which is to prepare and render fit for use the raw materials yielded by nature, is that which, in a more restricted sense, is called manufacturing industry, and the description and elucidation of the methods by which this object is attained is called technology, from *τέχνη* and *λόγος*. Taken in a general sense, this word would apply to all trades, arts, and manufactures, whatsoever; exclusive, however, of actual artist's work—notwithstanding the latter exceeds the industries in respect of the money-value of its productions—and exclusive, also, of such trades as tailoring, dress- and shoe-making, in which only certain commodities from materials that have been produced by manufacturing industry are worked up.

Mining and quarrying operations, as well as commerce, do not belong to technology, because the former deal with the getting to hand of naturally existing materials, and the object of the latter is either the carrying and distributing of the products from various parts of the world to the wholesale consumers, or the products of different kinds of one and the same country to the population thereof. The position of some industries is somewhat difficult to define in this sense, for while metallurgy and the knowledge of tools and machinery are undoubtedly an integral portion of technology, taken in its widest sense, the construction of railways, roads, and bridges, as well as shipbuilding, architecture, artillery science, &c., do not come within the province of technology, but belong either to engineering science or are specialities to be separately taught and described.

Technology is not a self-contained science which possesses its own peculiar doctrine and foundation; it simply borrows the principles and experience obtained by mechanical and natural sciences, always taking into consideration the best mode of applying these principles to the preparation of raw materials to become objects suitable for use. Technology is accordingly practical natural science, having for its object the reduction of manufacturing industry to the natural principles upon which it is based, and teaching the most advantageous methods and processes by which the raw materials are prepared for use. Raw products, which are either in the condition nature yields them, or which have already been in the hands of the manufacturer, are changed by the labour of men, either in their outward form only, or in their inner composition, and upon this distinction is based the division of technology into mechanical and chemical; the former division embraces such industries as have only for their object the changing, altering, and modifying the form and shape of the raw material, its inner composition remaining unaltered; as instances we quote the joiner and carpenter working in wood, the making of iron rails, sheath metal, and wire, the casting of iron, zinc, and alloys of copper into various objects, the spinning and weaving of various fibres, flax, cotton, jute, to become materials of greater value; also the manufacturing of paper from rags, of horn into combs, and bristles into brushes, belong to this section.

Chemical technology, however, deals with the operations by which a raw material is not only changed in its form, but *especially* as regards its nature: such, for instance, is the case with the extraction of metals from their ores; the conversion of lead into white-lead and sugar of lead (acetate of lead); the conversion of sulphate of baryta into chloride of barium and baryta white (permanent or Chinese white); the conversion of cryolite into sulphate of alumina, alum, and soda; the conversion of rock salt into sulphate and carbonate of soda; the conversion of carnallite and kainite into chloride and bromide of potassium, sulphate and carbonate of potassa; the conversion of copper into verdigris and sulphate of copper; the manufacture of paraffin and paraffin or crystal oils from peat, Boghead coal, and lignite; the preparation of kelp and iodine from seaweeds; the manufacture of stearine candles (stearic acid properly) and soap from oils and fats; the preparation of sugar and alcohol from starch; the conversion of alcohol into vinegar; the brewing of beer from barley and hops; the manufacture of pig-iron into malleable iron (puddling process), and the conversion of malleable iron into steel; the production of gas, coke, and tar from coals; the extraction from the tar of such substances as benzol, carbolic acid, aniline, anthracen, asphalte, naphthaline; the preparation of tar colours, as rosaniline, aniline blue, Manchester yellow, Magdala red, alizarine, iodine green, picric acid, &c. In very many cases, however, the preparation which the raw materials have to undergo before fit for use is simultaneously, or at least consecutively, a mechanical as well as a chemical process; for instance, in the manufacture of glass, sand, potash, Glauber salt (sulphate of soda), carbonate of soda, and limestone, are first fused together to form glass (a true salt, a silicate), and the soft mass is next wrought in various ways to form window-glass, tumblers, bottles, &c. Another instance is the manufacture of beet-root sugar, in the extraction of which the sugar itself is, it is true, not altered or changed in any way (this being as much as possible avoided), but the process of extraction is a combination of mechanical and chemical operations, the latter bearing chiefly upon the purification of the sugar, so as to free it from adhering foreign substances. The same observation applies to the manufacture of starch, to tanning operations, also to the various processes of dyeing and calico printing.

The ceramic arts (that is to say, the manufacture of earthenware, pottery, china, &c.), are generally included in chemical technology, although, in the production of the objects alluded to, the mechanical operations and fine art processes predominate. Pyrotechny (that is to say, the consideration of fuel and of its most useful and advantageous application to the production of heat, and the best mode of constructing furnaces, ovens, chimneys, &c.), is one of the most important parts of chemical technology.

From the foregoing the reader will readily perceive that it is scarcely possible to draw a sharp line of demarcation between the two divisions of technology (mechanical and chemical) alluded to. We therefore define chemical technology best by designating it as that branch of industrial science which treats of the processes and methods by which the nature of raw materials is usually altered.

In mechanical technology, machinery of various description, acting as the motive agent or for the exertion of great power, for the transference of movement or for the regulation thereof, and, lastly, as an actual implement, always plays a very prominent part, whilst in chemical technology its position is altogether subordinate; the great aim of improvement being chiefly directed towards:—1. Economisation of raw material, and, if by any possible means, its regeneration. 2. Economy of fuel. 3. Economy of time by improved and shortened methods of the various operations.

The ideal of a chemical manufactory is that there should be no real waste products at all, but only chief or main, and by-products. The better, therefore, the waste products are applied to good and advantageous use, the more nearly the manufactory will approach the ideal, and the larger will be the profit.

DIVISION I

CHEMICAL METALLURGY, ALLOYS, AND PREPARATIONS MADE AND OBTAINED FROM METALS.

General Observations.

Meaning of the term Metallurgy.

Ores.

Metallurgy, in a more restricted sense, embraces the doctrine of the various processes and operations, some of which are purely mechanical, others again purely chemical, by means of which metals and some preparations thereof are obtained on a large scale. We treat in the following pages almost exclusively of the chemical operations and processes by the aid of which ores are converted into metal or into some other product, and we shall therefore investigate the changes which the ore undergoes when submitted to different processes and operations resulting in the extraction of the metal. The number of the metals which belong to this category is not very large; the chief are iron, cobalt, nickel, copper, lead, chromium, tin, bismuth, zinc, antimony, arsenic, mercury, platinum, silver, gold. Excepting chromium and cobalt,* other metals are brought into the metallic state by means of smelting furnaces; but preparations of nickel, antimony, and arsenic are also obtained metallurgically. Magnesium and aluminium are as yet only prepared in chemical manufactories. Metallurgy, as a part of technology, treats chiefly of the physical and chemical principles upon which the extraction of metals from their ores is based; and includes, therefore, the description of the operations as based upon these principles. Only very few metals are found in the native, that is, metallic state: most of them occur as chemical compounds in the mineral kingdom, and these are termed ores; they are partly chemical combinations of the metal with metalloids, and partly consist of rock or gangue. Moreover, the term ore applies only in an industrial sense to those minerals which are worth the miner's working. Metals are found chiefly in combination with oxygen and sulphur. Metals occur in the ores in the following conditions:—1. In the native state, embedded in quartz, granite, gneiss, and other minerals,—gold, silver, platinum, mercury, copper, and bismuth. 2. Combined with sulphur, as, for instance, antimony, arsenic, and lead; these combinations being—(*a*) single ores, as, for instance, cinnabar (sulphuret of mercury), HgS; galena (sulphuret of lead), PbS; speisscobalt (a compound of cobalt metal and arsenic), $CoAs$; (*b*) double ores, as, for instance, sulphuret of iron and copper (peacock ore), $Fe_2S_3,3Cu_2S$; iron and copper pyrites, Fe_2S_3,Cu_2S; red silver ore, $Sb_2S_3,3AgS$. 3. Combined with oxygen, ores occur as—(*a*) basic oxides, as, for instance, hematite iron ore, Fe_2O_3; tinstone, SnO_2; red copper ore, Cu_2O; (*b*) as hydrated oxides, as, for instance, bog iron ore, $Fe_2O_3,3H_2O$; (*c*) as oxysalts, as for instance, malachite, $CuCO_3+CuH_2O$. 4. Combined with sulphur and oxygen, as for instance, red antimony ore, $2Sb_2S_3+Sb_2O_3$. 5. Combined with haloids, as for instance, the so-called horn silver ore, $AgCl$. 6. In combination with haloids and oxygen, as, for instance, horn lead ore, $PbCO_3+PbCl_3$.

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* Since 1862 M. Fleitmann has prepared chromium and cobalt on the large scale by a metallurgical process.

Dressing of Ores. Since the ores are not found in a state anything approaching to purity, but are mixed in the first place with what is technically termed gangue—rock, stone, or earth of any kind; and moreover, since very frequently the ores of different metals occur mixed together, they require, on being brought out of the mine, to be broken up and to be separated by mechanical means from the gangue and from other impurities. These operations as a rule are carried out on, or near, the spot where the ores are raised, and are designated by the name of dressing; the mechanical preparation of the ore is partly executed by hand, women and children being frequently engaged in picking out worthless stuff from among the minerals brought to bank; this sorting, accompanied commonly by the breaking up of the ore into small lumps, an operation executed by men with suitable hammers, is usually so carried on as to separate the ore into three kinds. The ore thus selected is placed in separate heaps, which may be classed as follows:—a heap containing rich ore of sufficiently good quality to be fit to be directly smelted; another heap contains ore which, previous to its being fit for the smelter, has to be further prepared, that is, purified from mechanically adhering impurities; while the third heap is devoted to such poor ore as would not pay the expense of the extraction of the comparatively small quantity of metal it contains. The mechanical operations alluded to are frequently effected by the aid of machinery, stamp and dressing mills, while very often water is used in completing the operations, its use being chiefly to remove the clay and earthy matter, sand, and pulverised rock from the specifically heavier mineral. **Preparation of Ores.** The dressing of the ores having been finished, they are fit for the smelting operations, but in many instances these cannot be proceeded with until the ores have undergone a preparation, consisting in some cases of an exposure to air—weathering; in others, again, in a heating of the ores, without access of air, designated calcination, or a heating with access of air, termed roasting.

The object of the exposure to air is in some instances to effect the weathering and subsequent loosening and separation (mechanically) of such minerals as slate, clay, and marly materials, which frequently adhere to certain kinds of iron and zinc ores; in other instances, again, the object of the exposure of metallic ores to air is the oxidation of iron pyrites, which is washed out by rain as sulphate of protoxide of iron. The object of the calcination of ores is partly to drive off water, carbonic acid, and bituminous materials; partly, also, to render the ores softer, and thus better fitted for the metallurgical processes by which the reduction to the metallic state is effected. The roasting of ores is carried on with the same object, but since the temperature is far higher, although not carried to the fusion of the ores, a more energetic chemical action takes place, and is in some cases promoted by the addition of common salt; moreover, the great object of the roasting of ores is to effect an oxidation of the same, accompanied in some, if not in all, cases by the volatilisation of various substances. As instances of the action of this process, we quote what occurs when magnetic iron ore, (Fe_2O_3,FeO), is roasted; the protoxide in this case is gradually converted into peroxide. When oxidation is accompanied by volatilisation three different things may happen.

1. A volatilisation of certain substances attended by oxidation. The ores which are chiefly submitted to this process are such as are combinations of sulphur, arsenic, and antimony, either jointly or singly, in which cases sulphurous and arsenious acids and oxide of antimony are volatilised, with the result that either pure metal is obtained, as is the case with cinnabar, which yields mercury, or the formation of metallic oxides and sulphates. The volatilised substances may be collected and utilised, as, for instance, the arsenious acid, and the sulphurous acid for the production of sulphuric acid, &c.
2. Volatilisation of certain substances by reduction is a less frequently occurring operation, chiefly carried on with some sulphates and arseniates of metallic oxides by heating the same with coal or charcoal, the result being the volatilisation of sulphur in the form of sulphurous acid and of arsenic *per se*.
3. Volatilisation by conversion into chlorides of metal. When an ore is roasted with the addition of common salt and free access of air, some partly volatile chlorides may be formed, as, for instance, in the extraction of silver from its ores by the European amalgamation process and M. Augustin's method.

Smelting of the Ores. As soon as the ores are sufficiently prepared by the methods just described, they are submitted to an operation having for its object the conversion of the ore into metal, or into some other combination thereof; the process, which is a true chemical operation, is called the smelting process. It rarely happens that only one kind of ore is operated upon; the more usual plan is to mingle richer and poorer ores together in certain quantities, so as to obtain a suitable mixture, attention also being paid to the various kinds of rock which accompany the ores, so as to obtain by the smelting process a proper slag; but if, as is more often the case, this end cannot be attained by the mixing of ores of different quality, it becomes almost always necessary to add other materials which either chiefly or solely act as fluxes, and also as reducing or converting agents, by promoting in various ways, to be presently more fully described, the separation of the metals from their ores. We distinguish accordingly between such materials as charcoal, coal and coke, lime, and common salt, which we term roasting materials (Röstzuschläge), and smelting or fluxing materials, such as quartz and various silicates, among which are hornblende, feldspar, augite, greenstone, chlorite-schist, slag; lime-containing minerals, as limestone, fluor-spar, gypsum, heavy-spar; minerals containing alumina, as, for instance, clay-slate and marl. Saline materials (admixtures) are also used, as potassa, borax, Glauber salt, and saltpetre; likewise metallic admixtures, as, for instance, iron used in the decomposition of cinnabar and sulphuret of lead; zinc, for the extraction of silver from lead; arsenic, in the preparation of certain nickel and cobalt ores; protoxide of iron (anvil dross), hematite iron ore, and manganese, used in the puddling process; certain saline admixtures, by which we understand, in this instance more especially, such blast furnace slags as contain a large proportion of protoxide of iron, and are applied in the process of puddling on account of the oxygen they contain; or, on the other hand, are used as so-called precipitating agents, on account of the iron they contain, *e.g.*, for the throwing down of lead from galena. The substances which act only as fluxes promote the separation of the metal, because the ore is more readily rendered fluid, thereby causing the particles of metal to unite more easily. According to their mode of action, fluxes can be brought under three heads, viz.:—1. Such as exercise no chemical action, but are only substances promoting fluidity, as, for instance, fluor-spar, borax, common salt, and various slags; 2. Such as at the same time exert a reducing action, as, for instance, a mixture of argol and saltpetre, so-called black flux; 3. Such as act as absorbents, either of acids or of bases: but this class belongs more properly to admixtures already alluded to above.

The Mixing of the Smelt. That operation, by which the ore and the materials required for the smelting process are intimately mixed together, often in previously weighed out quantities, is called the mixing, and the quantity which is to be used within a given lapse of time (generally 12 or 24 hours) is called the charge.

Products of the Smelting Operation. The following are the products which, generally speaking, are obtained by the smelting process :—1. Metals—Educts. The relative degree of the purity of these substances is indicated when gold or silver is alluded to by the title of their fineness (purity), fine gold or fine silver being understood as the perfectly pure metal; but as regards the metals not designated by the term noble, they are called raw or crude metal, while a higher degree of purity is indicated by refined. 2. Such products as are not present ready formed in the ore, but are the result of peculiar reactions which take place during the smelting process between the various ingredients submitted to the operation; these materials are, in most instances, ready for the market, and comprise the so-called hard lead which contains antimony, arsenic, and other impurities; arsenical preparations, as, for instance, arsenious acid, orpiment, realgar; and black sulphuret of antimony. 3. The preparation of educts is often accompanied by the formation of intermediate or by-products; if these happen still to contain a sufficient quantity of the metal operated upon to make it worth while to extract it, they are termed intermediate products; but if the reverse is the case they are called—4. Dross. Such intermediate products are often alloys; as, for instance, one consisting of silver, copper, and lead—the so-called *Tellersilber*—silver containing lead, consisting chiefly of lead, with a smaller or larger quantity of copper and some silver; so-called black copper, a mixture of copper, iron, and lead; sulphurets; arsenic alloys, so-called Speiss, as, for instance, the cobalt and nickel compounds obtained in smalt works, chiefly consisting of arsenical nickel; carburetted metals, as, for instance, pig-iron and steel; oxides, as for instance, litharge (oxide of lead).

Slags. The material which usually passes by this name exhibits, when cold, an enamel or glass-like appearance, and is generally made up of various combinations of silica with earths, such as lime, magnesia, alumina, and metallic oxides, as the protoxides of iron and manganese. The slags are formed during the smelting process because the raw materials, and the various substances employed, contain the elements for their formation. The functions of the slag during the smelting process are rather important, serving to protect the particles of metal, or of sulphuret of metal, from the oxidising action of the blast, and promoting the adhesion and union of the particles. Slags are applied in some smelting processes as a flux; and if they should still contain a sufficient quantity of metal, they are added to another batch of ore to be operated upon. As regards their composition and nature, they are classified according to the quantity of silica they contain as sub-, mono-, bi-, and tri-silicates. The proportion which the oxygen of the silica bears to that contained in the bases is as follows :—

Subsilicate	3 : 6
Monosilicate	3 : 3
Bisilicate	6 : 3
Trisilicate	3 : 1

Slags are either vitreous or crystalline. It very frequently happens that from the latter kind portions of silicates separate, which, as regards their chemical and mineralogical characters, agree with minerals met with in nature, such as augite, olivine, Wollastonite, mica, idocrase, chrysolite, feldspar, &c. Generally speaking, the mixtures of monosilicates produce slags which are very fluid, and apt to consolidate rapidly while cooling, while the mixtures of bi- and tri-silicates produce slags which have the opposite properties, being pasty and tough.

The following properties and constitution denote that the slags are suited to the smelting process:—1. The specific gravity of the slag while molten should be less than that of the product (metal) it is desired to obtain, in order that the slag may cover the surface of the molten metal. 2. The slag should be homogeneous throughout the duration of the process of smelting; since the contrary would denote an abnormal working of the operation. 3. The slag should melt readily, and thus admit of the particles of metal readily sinking downwards as a consequence of their higher specific gravity. 4. The chemical composition of the slag should be so regulated as to prevent them exerting any decomposing action upon the metal.

IRON.

($Fe = 56$; Sp. gr. = 7·7.)

Iron: Its occurrence. Iron is the most important and most useful of all metals. Its application is most intimately connected with all branches of industry, and almost all the wants and requirements of common daily life. The reason of this very extended employment of iron is due, partly to its being plentifully and even superabundantly met with in nature, but partly, if not chiefly, in consequence of the great ease wherewith this metal, during its reduction from the ore, assumes various modifications and exhibits different characters, each possessing some special feature of usefulness. Although the number of minerals which contain iron is very great, comparatively few are used in practice for the extraction of the metal. Those that are used are all oxygen compounds of iron, and chiefly what are technically known to ironmasters and the trade as *ironstones*.

The following is a list of the minerals termed "ironstones":—

1. Magnetic iron ore, ($Fe_2O_3,FeO=Fe_3O_4$), the richest of all iron ores (it contains upwards of 72 per cent. of iron), is pretty largely found, especially in Russia, Norway, and Sweden, in the crystalline schistose rock. The celebrated Dannemora (Sweden) iron is obtained from this ore. It not unfrequently happens that this mineral is more or less mixed with iron pyrites, galena, copper pyrites, apatite (chiefly phosphate of lime), and other minerals, which, by their presence, impair the good qualities of the magnetic iron ore as a mineral.

2. Hæmatite iron ore, red ironstone, (Fe_2O_3), contains about 69 per cent. of iron. This mineral occurs in seams and veins in the older geological formations, often embedded in gneiss and granite. It is also met with in the metamorphic rocks, and is frequently called glassy head, owing to its external lustre; also bloodstone, on account of exhibiting, when scratched with a file or a knife, a deep red-coloured streak. When this ore is found mixed with silica, it is called siliceous ironstone; when occurring along and mixed with alumina, it is called red aluminous iron ore; mixed with lime, the ore is known as minette. The quantity of iron present in these ores varies, of course, considerably. This ore occurs in crystalline state, in especially large quantities in the Island of Elba, and ores of the same kind, but different in quality, are found in England and Ireland, Saxony, and many parts of Germany. They are, in all cases, especially as regards the first-named country, largely applied, *e.g.*, Lancashire (Ulverston and Barrow-in-Furness).

3. Spathose iron ore, ($FeCO_3$), with 48·3 per cent. of iron. This ore, which occurs in great variety, is, indeed, the chief iron-stone, often containing carbonate of protoxide of manganese in larger or smaller quantity. This ore is often met with in a globular or kidney-like shape, and hence called kidney iron; in mineralogy, spherosiderite. The ore bears a great many other names, derived from some peculiarities in its composition; for instance, it is known and very largely worked in Scotland as black-band, owing to its being mixed with carbonaceous and bituminous matters, and alternating with seams of coal. It is known, also, as clay-ironstone, being then mixed with more or less argillaceous matter, and occurring in enormous quantities in that condition in Cleveland and Rosedale (Yorkshire), in Wales, and also on the Continent in various countries.

4. When the last-named ore is acted upon by air and water containing carbonic acid, a secondary ore is formed, known as brown ironstone (partly Fe_2O_3,H_2O, partly $Fe_2O_3,3H_2O$). In mineralogy this ore is named according to its varying physical properties, as follows:—Lepido-crocite, needle-iron ore, pyrosiderite, and stilpnosiderite. As may be expected,

this mineral is often mixed with carbonate of lime, silica, alumina; the yellow ironstone being a variety of the aluminous kind. Bauxite may in some instances range along with this kind of ore, when that substance consists of an intimate mixture of alumina and peroxide of iron.

5. Pea-iron ore, in smaller or larger globular-shaped particles, formed of concentric layers, containing either an intimate mixture of silica, protoxide of iron, and water, or brown iron ore and siliceous clay. The origin and mode of formation of this ore are unknown. It occurs in France and in the South-West of Germany.

6. Marsh iron ore, limonite, met with in parts of Europe, generally those which are only little elevated above the sea level, and more especially in or near moors and marshes, peat bogs, &c.; in some parts of the Netherlands, Denmark, Sweden, and North Germany, and also in the United Kingdom to some extent. This ore owes its origin to the action of decaying vegetable matter upon water containing carbonate of protoxide of iron in solution. The ore is met with in irregularly shaped lumps, as hard sometimes as pebbles, but also in a soft and spongy condition; its colour is brownish, or black, and it consists of protoxide of iron, oxide of manganese, phosphoric acid, organic matter, and sand. According to M. Hermann, however, the ore contains hydrated peroxide of iron, hydrated oxide of manganese, phosphate of peroxide of iron, tribasic crenate of peroxide of iron. This ore is in some instances largely used for the manufacture of cast-iron objects (especially for domestic and ornamental uses), on account of its yielding an iron of great fluidity, which fills the moulds very completely, giving sharp-figured castings. This condition is due to the presence of the phosphorus in such iron; but the presence of this element also causes the pig-iron made from this ore, if puddled, to yield a wrought-iron which is both cold- and red-short.

7. Franklinite, ($Fe_2O_3[ZnO,MnO]$), containing 45 per cent. of iron, 21 per cent. of zinc, and 9 per cent. of manganese. This ore occurs in New Jersey, U.S., and is there employed both for the extraction of iron and zinc.

Iron is also obtained from rich slags, which often contain, in the shape of protoxide of iron, an amount varying from 40 to 75 per cent. of that metal; they are employed in the puddling process. The scraps of iron resulting from various operations, old iron, and waste pieces of the metal, are usefully applied, either alone or with the ores, to be re-converted into metal.

Taken from a metallurgical point of view, iron ores are distinguished as reducible easily or with difficulty (convertible into metal readily, or fusible with difficulty). To the former class belong all those ores which, while being submitted to a preliminary roasting, become porous, and hence more readily penetrable by the reducing gases present in the blast-furnace; and, as a consequence, more rapidly reduced and molten. The spathose iron ore and brown iron ore belong to this class; the former because on roasting it loses carbonic acid, while the latter loses water. Magnetic iron ore, and hematite iron ore in all its varieties, are reducible with difficulty.

a. PIG OR CRUDE IRON.

Extraction of Iron from its Ores.

The extraction of iron from its ores is chiefly based upon the two following properties:—1. While particles of pure or nearly pure iron are infusible even by the heat produced in the blast furnace, they are possessed of the property of agglutination to larger masses; in other words, the property (possessed by iron and only a few other metals) of welding together at a bright red heat.

2. Iron is capable of uniting, while exposed to a high temperature, and in the presence of an excess of carbonaceous matter or gases containing carbon, with that metalloid, forming with it an easily fusible compound, viz., a carburet of iron, the so-called pig- or cast-iron.

The direct manufacture of malleable iron from iron ores was in former times a very usual proceeding, and is yet carried on to a small extent in some parts of Europe (Styria, Andorra, Sardinia, and Sicily), and far more so in Hindostan; but this method, known as the Catalan process, is wasteful, and although it yields iron of excellent quality, it also requires ores of great richness. The process is not suited to meet the large demands now made for iron; with these trifling exceptions all iron at the present day is obtained by the production first of pig-iron, which is afterwards converted into malleable iron by the puddling process.

The operations by which iron is extracted from its ores are:—calcination or roasting, and smelting. The object of the first-named operation is the removal from the ore of such substances as water, carbonic acid, carbonaceous matter (as present in the black-band ironstone); also the conversion of any protoxide into peroxide, because the latter is less apt to become absorbed by the slag, and to promote the porosity of the ore. The calcined ores are next broken up to lumps of suitable size by means either of stamping mills or cylinders, or by machinery specially made for the purpose on the principle of quartz and stone crushers; after this has been done the ores are mixed, rich and poor together, in such proportions as have been found in the experience of the workmen to yield the best quality and largest quantity of iron.

Theory of the Iron Extraction Process. The ores having thus been mingled, constitute a mixture made up chiefly of an oxide of iron and of gangue (silica) or lime; carbonaceous matter is added thereto, and the mass is submitted to a strong heat, the result being the reduction of the iron to the metallic state, according to the following equation:—

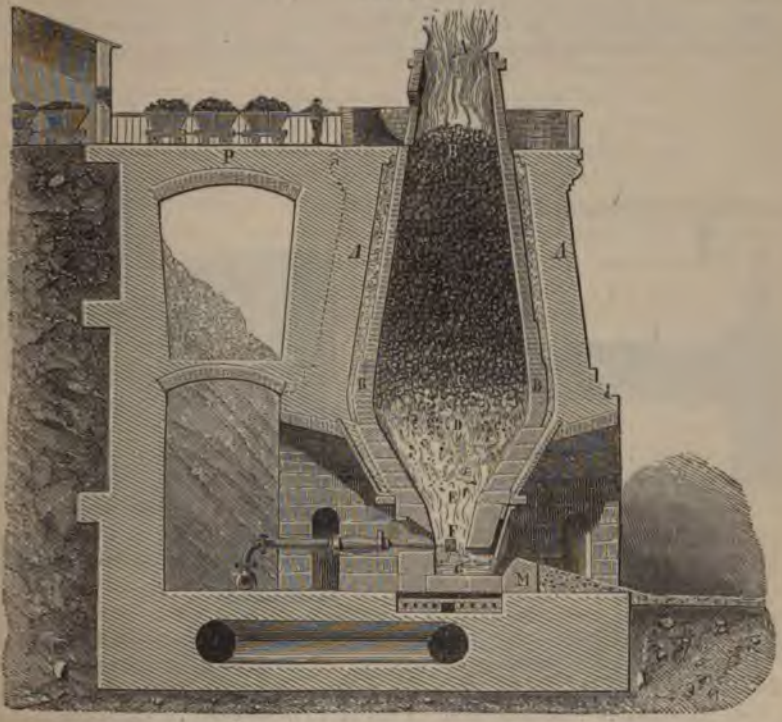
$$Fe_2O+_33C=3CO+2Fe;$$

the action, therefore, of coal is to serve as fuel and at the same time as reducing agent along with carbonic oxide and carburetted hydrogen; if, however, the operation were performed by simply mixing the broken up ores and coal or coke, and submitting this mixture to the smelting process, the iron would be obtained in a finely divided and spongy condition; and in order to procure the union of the particles of metal so as to form a molten mass previous to the smelting operation being proceeded with, certain substances which have the property of forming with the gangue a readily fusible glassy mass are added. The substance added is technically known as slag, and it serves not only the purpose just mentioned, but also that of withdrawing and absorbing from the ore such materials as might injure the quality of the iron; and, lastly, the slag being by far specifically lighter than molten iron, floats on the surface and protects the metal from the oxidising action of the air blown into the furnace. Slag is a mixture of various silicates; in some instances the ore itself contains, along with the oxide of iron, the constituents necessary to form a good slag, but in most instances ores require the addition of such materials as will form, with the constituents (excepting the iron oxides), a proper slag; thus, for instance, if silica were wanting, quartz or sand would be added; and if bases were wanting, lime-stone or fluor spar (fluoride of calcium) would be added. The slag should become fluid at or about the same temperature as the metal. The mixture of ironstone and slag-forming material is called a batch, and is so arranged as not to contain above 50 per cent. of iron. When iron in the molten condition and carbonaceous matter (coal, coke, or charcoal, although the latter is very rarely used) come in contact, as is the case during the smelting process just alluded to, the molten metal dissolves a large proportion of carbon; but when the metal cools a portion of the carbon separates in the crystalline form; this is termed blast-furnace graphite: another portion of the carbon remains, however, in chemical combination, and it is therefore evident that the smelting of iron ores produces an iron—pig or crude iron—which contains carbon, and is, therefore, not a pure metal.

Blast-furnace Process. At the present day the extraction of iron from its ores (smelting) is chiefly carried on either in what are termed blast-furnaces or blowing-furnaces. These contrivances are not essentially different from each other as regards their action, but their arrangement and construction is so far different that the slag from blast-furnaces, working as they do with what is termed an open breast-plate, runs off continuously, while the slag from the blowing-furnace has to be cleared from time to time when tapping the metal.

Description of the Blast-furnace. A blast-furnace is an oven showing on the exterior a heavily made wall (Fig. 1, A, the outer wall), having a height of from 14 to 35 metres; the inner lining is made in the shape of two truncated cones placed together at their bases; the brickwork (fire bricks) which constitute this double cone-like structure, B, is surrounded by a casing made up of broken scoriæ or refractory sand, which is enveloped by the external coating of heavy masonry; the sand is a bad conductor of heat and admits also of space being allowed for the expansion by heat of the interior structure. The portion of the internal cone extending from B to C is called the shaft, or chamber, while the portion which extends from D to E is named the boshes; the part of B where the diameter is greatest is called the belly or upper part of the boshes. Below the boshes at F, the space is gradually made narrower, and called the throat, or tunnel hole, the lower part of which is intended for collecting the molten metal, and named the crucible or hearth; this portion of the blast-furnace is the most important, because the smelting process goes on in it; the crucible is provided with two opening placed opposite to each other, and containing conically-shaped tubes (see Fig. 2) called the tuyeres, ending in what are termed the nozzles or nose pipes, or the blast pipes; these tubes serve to convey the air necessary for the furnace. As shown in the engraving, the admission of air to the nozzles is re-

FIG. 1.



gulated by a valve. The upper open end of the furnace at A is called the mouth or furnace top; through this opening the fuel and mixture of ore and flux are put into the furnace, which is (as also shown in Fig. 1) situated on or near the slope of a hill, so as to have ready access to the mouth by means of the bridge for conveying the materials to the furnace-top. The lower part of the hearth is prolonged towards the front, thus forming the breast-pan, which is enclosed by the dam-stone, M; this stone is somewhat removed at one side from the wall, thereby forming a slit, which is technically called the tap-hole; this is the discharge aperture; while the smelting is going on this aperture is closed up with fire-clay, which is removed when it is required to withdraw the slags or tap the crucible, that is to say, discharge the molten metal. The dam-stone is protected by an iron plate. Three only of the sides of the hearth are continued to the stone constituting the bottom of the arrangement; the fourth is merely brought to within a certain distance of the base, where it is supported by strong girders of cast-iron firmly fixed into the masonry of the walls, and on which rests a heavy block of sandstone called the tymp (see Fig. 1), which is supported by a very heavy and stout piece of iron called the tymp iron.

FIG. 2.

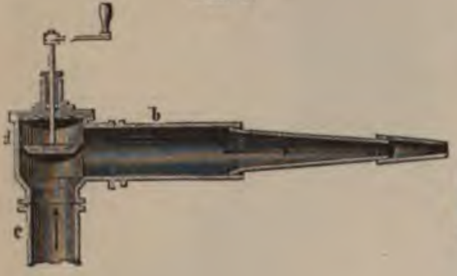
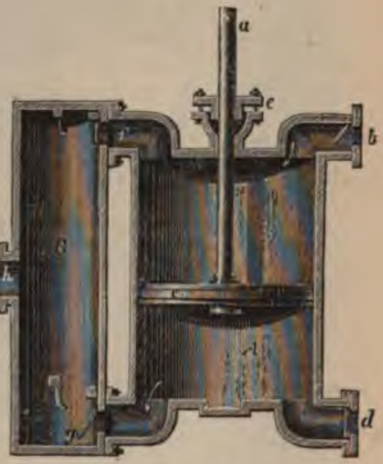


FIG. 3.



The Blowing Engine and Blast. In order to provide the necessary quantity of air for the blast-furnace, a blowing engine is attached; this is now almost exclusively constructed upon what is termed the cylinder principle, which in one of its most convenient forms is delineated in Fig. 3. The cast-iron cylinder, A, contains a piston, *c*, which by means of the piston rod, *a*, passing air-tight through the stuffing box, *e*, can be moved upwards and downwards; at *b* and *d* the cylinder is in communication with the outer air, and by means of *f* and *g* it communicates with the chest, E. The openings alluded to are provided with self-acting valves for regulating the flow of air, which is conveyed through *i* into the pipes communicating with the blast-furnace. In order to regulate the blast, a large sheet-iron vessel, in construction very similar to the gas-holders of gas-works, and acting on the same principle, is applied. The application of hot air for the blast is one of the most important improvements in the manufacture of iron, since, in this way, a decreased consumption of fuel, to the extent on an average of 0·366 (from ⅓ to ⅔), has been obtained; while, moreover, the absolute gain in the production of iron amounts to about 50 per cent. It is also stated by many iron-masters that the furnace is more readily and regularly worked; but this statement is discredited by others, who aver against the hot blast that disturbances arise more frequently in the regular course of working; also, that the very high temperature in the crucible causes the rapid destruction of the fire-bricks, and consequently impairs the time of what is technically termed the campaign, that is to say, the duration of the fabric of the blast-furnace. The air intended for the hot blast is heated either by the gases given off by the blast-furnace, or by means of separate fire-places which heat a pipe apparatus, or lastly by means of Siemens's regenerative furnace system. This system consists in first conducting the gases of the blast-furnace through a fire-brick built space filled with fire-bricks loosely piled together, which becoming thoroughly red-hot are in that condition capable of heating the cold air previous to admitting it, care being taken to shut off the blast-furnace gases; by this means the air can be heated to a temperature very far exceeding that which is attainable by passing the air through iron tubes, these not admitting without serious injury of being heated to so high a temperature in contact with air. The hot blast air is heated to from 200° to 400° C.; blast furnaces fed with coke as fuel require per minute of time from 2000 to 4000 cubic feet of air.

Course of the Smelting Process.

The blast furnace is worked in the following manner:—The furnace is first heated by igniting in it a quantity of wood. When this has rendered the oven thoroughly dry, the fuel intended for use in the course of the continued process is put in (this fuel used to be in Germany wood charcoal, but at the present time there, as in England, coke is employed, or sometimes anthracite; common coals are rarely used); the furnace is at first entirely filled with fuel, and when quite full the blast is turned on and a beginning made with the charging of the mixture of ore and flux, alternating with fresh fuel. By the burning of the fuel, and the fusing of the ore and flux, the layers sink downwards, the silica fuses, forming, while combining with the earths and some of the oxides present in the ore, a slag which is commonly coloured by the presence therein of oxide of iron, while the iron reduced to the metallic state, and semi-fluid at first, combines with carbon to form readily fusible pig-iron; the molten metal collects in the hearth or crucible; the fused slag floats on the top of the metal, but is run off over the dam-stone. The molten metal is tapped off about twice every 24 hours, or as soon as it appears to reach the height of the dam-stone. The aperture here alluded to, and closed provisionally by means of fire-clay, is opened by the piercing of the latter, while the molten metal is conveyed through channels made in the sand to the moulds, also formed in the same material; during the operation of tapping, the blast is shut off. Crude iron cast in the shape of cakes is called lump-iron, and when run into bars, pig-iron. The campaign, that is, the operation of smelting with the same furnace, often lasts many years; it is, in fact, continued until the oven or blast furnace becomes worn out.

Chemical Process going on in the Interior of the Blast Furnace.

The chemical process which is going on in the interior of the blast furnace when at work (technically, while in blast) differs considerably in different portions of the vertical section. The annexed Figs 4 and 5 represent the interior of a blast furnace exhibited in perpendicular section, and filled with alternate layers of fuel and mixed ore and flux, the latter being indicated by the narrower, the former by the wider layers. Counting from the surface of the fluid slag, *f f*, up to the mouth of the furnace the interior may be divided into five zones or regions, viz.:—

1. The first heating zone, *a b*.
2. The reduction zone, *b c*.
3. The carburation zone, *c d*.
4. The melting zone, *d e*.
5. The combustion zone, *e f*.

In the upper part of the furnace, the first heating zone, the materials become warmed and are rendered thoroughly dry, but they hardly become hotter than a low red heat. The reduction zone is the largest in extent. In the lower part of the shaft of the furnace, and especially towards the belly, the oxide of iron is, by the action of the reducing gases, first converted into protoxide of iron and next into metal. The reducing agents present in this zone are—carbonic oxide, carburetted hydrogen gas, and hydrocyanic acid gas (cyanide of hydrogen), or vapours of cyanide of potassium; at a certain part in this zone the iron is present as malleable iron. Deeper down in the furnace the carburation zone is met with; here the combination between the iron and carbon takes place, producing a more or less steel-like and somewhat caked iron, which, when sinking, enters the melting zone and is saturated with carbon and entirely brought to the state of pig-iron. At the portion forming the combustion or oxidation zone, which is, as compared with the other zones, only of very small extent, the air from the blast enters the furnace through the nozzles, and meeting with incandescent coke at the highest possible white heat, causes the formation of carbonic acid, but this gas in passing upwards through other layers of incandescent fuel becomes reduced to carbonic oxide ($CO_2 + C = 2CO$); by the combustion of the hydrogen contained in the fuel, water is also formed, which, along with the aqueous vapour con-

Fig. 4.

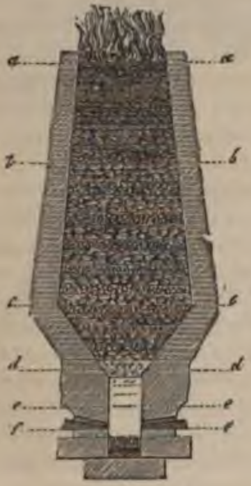
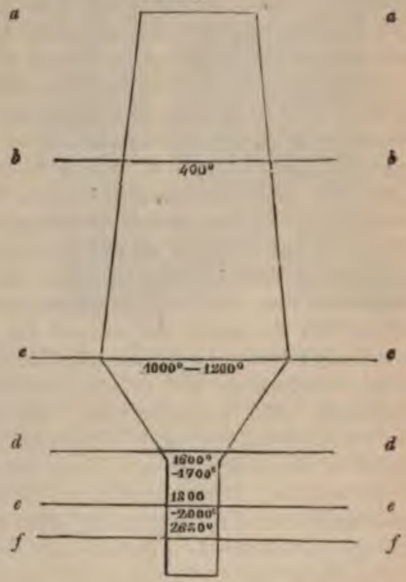


Fig. 5.



tained in the air of the blast (recently it has been tried to eliminate this aqueous vapour by passing the air previous to reaching the nozzles through concentrated sulphuric acid) is decomposed by the enormous heat of the middle portion of the furnace as well as by the presence of carbon, forming hydrogen and oxygen, the former of which enters into combination with the carbon, forming carburetted hydrogen, while the latter combining with the same element produces carbonic oxide. The nitrogen present in the coke, as well as a portion of the nitrogen present in the air of the blast, combines with the carbon, forming cyanogen (either as cyanide of some metal or as cyanide of hydrogen).* The reducing gases meeting with the ores cause the oxides present to be converted into metal, while the gases remaining (the blast furnace gases) escape from the mouth of the furnace. The reduced iron combines, while sinking downwards, with carbon, forming the crude metal, and fuses in so doing; the union of the particles being promoted by the slag. As soon as the iron reaches that portion of the furnace where the heat is strongest, the carbon contained in the metal begins to exercise its reducing action upon such substances as alumina, lime, silica, &c., which in the reduced, or metallic, state combine with the iron.

Recent researches have proved that the copious production of hydrocyanic acid generated by the process going on in the blast furnace greatly and very essentially assists the reduction of the ores; that compound of course combines with the alkalies and alkaline earths contained in the fuel and other materials. It has been surmised that the crude iron is not solely a carburet of that metal, as might be produced by the decomposition of cyanide of iron, but, in addition to a small quantity of that body, contains also nitride (a nitrogen compound) of that metal. In support of this view the fact is brought forward, that Dr. Wöhler, of Göttingen, found many years ago that the cubical crystals of what was considered to be metallic titanium, and found in the blast furnace slag, turned out to be a compound of nitride of titanium and cyanide of that metal. In order to give some idea of the large quantity of metallic cyanides generated by the blast furnace process, we briefly quote from the researches made on this subject by Drs. Bunsen and L. Playfair, that an English blast furnace, fed with coal as fuel, produced daily a quantity of 225 pounds. M. Eck, who made some researches on this subject at Königshütte, in Upper Silesia (Prussia), discovered the formation of both cyanide and sulphocyanide of potassium, and he found by calculating from the quantity of potassa contained in the ores, flux, and fuel, a daily production of 35½ pounds of cyanide of potassium. The reduction of alumina and silica to aluminium and silicium also takes place in the melting zone.

Temperature in the Blast-furnace at Different Points.

Fig. 5 exhibits the temperature prevailing at the limits of each zone. The temperature of the combustion zone would be far higher than happens to be the case were it not that, by the conversion of carbonic acid into carbonic oxide—that is, the absorption, or more correctly vaporisation of carbon—a considerable lowering of temperature (in other words, absorption of heat which becomes latent) is produced. It should be remembered that here the volume of the carbonic acid is also doubled, while this reaction is taking place, and that process of course also absorbs heat.

Taking into due consideration the fact that, under the most favourable conditions only 16·55 per cent. of the fuel supplied to a blast furnace is usefully consumed, while no less than 83·45 per cent. escapes from the mouth in the shape of combustible gases, it cannot excite any wonder that the idea arose of utilising these gases; this idea has actually resulted in various useful ways, as, for instance, for the fusion and puddling of the iron, for the refining and cleansing by welding of the iron, for the heating of the blast, the roasting of the ore, and the drying and carbonisation of the wood.

Blast-furnace Gases.

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* According to the view of M. Berthelot [1869] there is in this instance first formed acetylide of potassium, C_2K_2, which then combines directly with nitrogen to form cyanide of potassium, $2(CNK)$.

Application of these Gases to the Manufacture of Sal-ammoniac. The application of the gases to the useful purposes just mentioned does not exhaust the list of such applications. Drs. Bunsen and Playfair found that the gases emitted by blast-furnaces fed with coal as fuel contain such a large amount of ammonia that the presence of that gas in the lower parts of the blast-furnace is even perceptible to the smell. These eminent *savants* proposed to convey the gases previous to being used as fuel through a chamber containing hydrochloric acid gas; the solution of sal-ammoniac thus obtained should be run into the pan of a suitably constructed reverberatory furnace; and a small portion of the current of gas, after having been ignited, being carried over the surface of the liquid, the evaporating process can be regulated so as to obtain a continuous stream of a concentrated solution of sal-ammoniac as a metallurgical by-product. Experiments instituted at the Alfreton Iron Works (blast furnace) proved that in this way about 2·44 cwts. of sal-ammoniac could be produced daily without any great expense and without any interference with the process of iron manufacture. The formation of sal-ammoniac is intimately connected with the formation of cyanogen just spoken of. When cyanide of potassium comes into contact with aqueous vapour, it is decomposed into ammonia and formiate of potassa—

$$(KCN + 2H_2O = NH_3 + CHKO_2);$$

the reverse reaction, that is to say, the withdrawal of all oxygen in the form of water, from formiate of ammonia would result in the formation of cyanide of hydrogen—

$$[CH(NH_4)O_2 - 2H_2O = CHN].$$

Crude Iron. Cast-Iron. The iron obtained by the blast-furnace process is impure, and therefore called crude cast-iron; it contains carbon (in the shape of graphite as well as in a state of intimate chemical combination with iron as a carburet of that metal), silicium again as so-called silicium graphite and as a siliciuret of iron, sulphur, phosphorus, arsenic, and aluminium. The colour and physical properties of the iron are determined by the quantity of carbon it contains. Formerly the more or less deep colour of the crude iron was believed to be dependent upon the larger or smaller quantity of carbon the iron contained, and accordingly, the deepest coloured metal was supposed to contain the largest, and the least coloured iron, the smallest quantity of carbon; investigations have, however, satisfactorily proved that it is not so much the quantity as the manner in which the carbon (likewise the silicium) is present that determines the quality. The fact is, that with carbon and silicium a portion only is chemically combined with the iron, while the largest proportion of these metalloids is only mechanically mixed with the metal, being, as already stated, present in the form of graphite (graphitic carbon and silicium). According to the researches of M. Frémy and others, it is probable thst crude iron frequently contains nitrogen, and that the presence of this element influences the quality of the metal; but this view is not endorsed by MM. Caron, Gruner, and Dr. Rammelsberg. There are two chief qualities of crude iron in the trade, viz., *white* and *grey* coloured.

White Cast-Iron. White cast-iron is distinguished by its silvery white colour, hardness, brittleness, strong lustre, and higher specific gravity, which ranges from 7·58 to 7·68. Sometimes this kind of iron happens to contain prismatic crystals visible to the naked eye, and such iron is then called spiegeleisen, or crystalline pig (crude steel iron.) This variety of iron may be viewed as a combination of CFe_6, or, more accurately stated as $Fe_6C + Fe_8C$, with 5·93 per cent. of C. If the structure of the white cast-iron is radiated and fibrous, while the colour is bluish-grey, the metal is known as white pig-iron with a granular fracture. When the white colour disappears still more, and the fracture becomes jagged, such a metal holds a medium between white and grey pig, and is therefore called porous white pig.

Grey Cast-Iron. Grey cast-iron exhibits a bright grey to deep blackish grey colour. Its texture is granular or scaly; its specific gravity averages about 7, consequently less than the white variety, and the grey iron is also less hard. When pigs happen to contain both grey and white iron in portions only, or dispersed through their entire mass, such metal is called half-and-half iron, and is specially applicable to foundry purposes. The chemical difference between white and grey cast-iron is due to the fact that the former only contains chemically-combined carbon (from 4 to 5 per cent), while the latter contains from 0·5 to 2 per cent. of this element in the combined state, with rather more than that amount mechanically mixed, viz., from 1·3 to 3·7 per cent. As regards the melting-point of cast-iron, the white variety fuses at a lower temperature and more easily; but the grey cast-iron possesses far greater fluidity. Crude cast-iron is not malleable, and cannot be welded or forged; when made red-hot, it becomes very soft—so soft that it can be cut with a saw such as is used for sawing wood; but when placed on an anvil and hammered, this iron breaks into fragments even when red-hot. Grey cast-iron is the best, and, in fact, only suitable kind of crude iron to be used for making iron castings. The perfect fluidity of this metal when molten causes it to fill the moulds well, and to yield excellently sharp and well-defined forms. White cast-iron, on the contrary, is not used for iron-foundry purposes, because, while solidifying, it warps, and the surface becomes concave. Grey cast-iron can be filed, cut with the cold chisel, turned upon the lathe, and planed. White cast-iron is too hard to admit of any such operations being performed upon it. Grey cast-iron, molten and then suddenly cooled, is converted into white cast-iron; on the other hand, white cast-iron, molten at a very high temperature (heated far above its melting-point), and cooled very slowly, becomes converted into grey cast-iron.

The quality of the iron produced by the blast-furnace process does not so much depend upon the ores and other materials used. In this respect the temperature is of far greater importance. It would appear that after every fresh charge there is at first produced white cast-iron, which is only converted into grey cast-iron by a very much increased temperature. If the reduction of the ore to metal—care being of course taken to have a proper proportion of ore and the other materials—proceeds regularly, the furnace is said to be in a healthy state of working. Under such conditions, the slag, which contains only very little protoxide of iron, is never deeply coloured. If fuel were not supplied in proper proportion and the ore to prevail, the reduction would probably be imperfect and the slag a deep colour, in consequence of the presence of a large quantity of protoxide of iron (colour of dark green bottle glass). Such a condition of working is termed irregular. When, in consequence of an excess of fuel, the heat in the furnace becomes very great, that condition of working is termed hot, and only grey cast-iron is formed.

The results of the chemical analysis of some varieties of crude metal may elucidate the general composition of cast-iron: the under-mentioned samples are:—1. Spiegel iron, made from 14 parts of spathose ironstone and 9 parts brown iron ore (Hammerhütte). 2. White pig-iron, with a granular fracture, from Styria. 3. White pig. 4. Half-and-half pig. 5. Grey cast-iron (from brown iron ore and charcoal). 6. Grey cast-iron, from brown iron and spathose iron ore mixed. 7. Grey cast-iron, from ochreous brown iron ore and coke. The sign — indicates that no search or testing was made for the substance; the sign 0 indicates that the substance was not found.

	1.	2.	3.	4.	5.	6.	7.
Combined carbon ..	5·14	4·920	2·91	2·78	0·89	1·03	0·58
Graphite	0	0	0	1·99	3·71	3·62	2·57
Sulphur	0·02	0·017	0·01	0	—	—	—
Phosphorus..	0·08	0	0·08	1·23	—	—	—
Silicium	0·55	0	0	8·71	—	—	—
Manganese	4·49	0	1·79	0	—	—	—

The results below are those obtained by M. Buchner, while examining the quantities of carbon and silicium contained in crude iron: 1, 2, 3, 4, are Spiegel iron, almost or quite crystalline; 5, 6, porous white pig.

	1.	2.	3.	4.	5.	6.
$C\gamma$	4·14	3·80	4·09	3·75	3·31	3·03
$C\beta$	—	—	—	—	—	—
Si	0·01	0·01	0·26	0·27	Spur	0·15

7, 8, 9. White, very bright, crude iron. 10. White pig. 11. Half-and-half pig. 12. Strongly mixed half-and-half.

	7.	8.	9.	10.	11.	12.
Cγ	3·40	2·70	2·13	3·60	3·34	2·72
Cβ	—	—	—	—		
Si	0·14	0·12	0·10	0·66	0·10	0·20

13. Less strongly mixed half-and-half. 14, 15, 16. Grey cast-iron. 17. Coarse-grained cast-iron. 18. Over-coaled black-greyish cast-iron.

	13.	14.	15.	16.	17.	18.
Cγ	2·17	1·35	1·18	0·71	0·38	0·26
Cβ	2·11	2·47	2·42	2·79	3·28	3·83
Si	0·09	0·70	0·66	1·53	1·62	0·59

Statistics concerning the Production of Crude-Iron. The present (1870) production of crude iron (pig-iron) amounts to rather more than 200 millions of hundred weights. Of this quantity the under-mentioned countries produced :—

United Kingdom of Great Britain and Ireland	115,000,000 cwts.
France	24,500,000 "
North America, U.S.	20,200,000 "
Prussia	16,300,000 "
Belgium	8,900,000 "
Austria	6,750,000 "
Russia	6,000,000 "
Sweden	4,500,000 "
Luxemburg	1,100,000 "
Bavaria	732,000 "
Saxony	280,000 "
Würtemburg	138,000 "
Baden	16,000 "
Hesse	250,000 "
Brunswick	90,000 "
Thüringia	18,000 "
Australia	2,000,000 "
Italy	750,000 "
Spain	1,200,000 "
Norway	500,000 "
Denmark	300,000 "
	209,524,000 cwts.

Having a value of about 97·5 million pounds sterling.

Iron-foundry Work. Re-melting Crude Cast-Iron. For the manufacture of iron castings a somewhat mixed grey iron is employed, because its qualities best suit the purpose. These qualities are closeness of grain, strength, a capability to well fill the moulds, coupled with sufficient softness to admit of boring, filing, &c. Although iron castings can be made directly from the tapping of the blast-furnace, it is found advantageous and preferable in practice to re-melt the pigs. This operation is carried on in crucibles in a cupola furnace, or in a reverberatory furnace. Crucibles (made of plumbago or fire-clay) are only used for making castings of small size. The quantity of iron melted in crucibles does not usually exceed five or eight pounds.

Shaft or Cupola Furnace. For the purposes of the iron-foundry, the shaft or cupola furnace, represented in Figs. 6 and 7, is more generally used. The cupola furnace is in form cylindrical, and from 2·5 to 3·5 met. high. The pig-iron, previously broken up to lumps of suitable size, and the fuel, which may be either coke or wood charcoal, are placed in alternate layers in the shaft A; the openings *c* and *d* are intended for the insertion of the tuyeres connected with the blast. The opening leading to the spout, B, is closed during the progress of the melting; as soon as the molten iron reaches the orifice at *a*, this opening is closed by means of fire-clay, and the tuyere first placed in *a* is transferred to the opening *d*. The molten metal is either conducted by the aid of channels direct to the moulds, or tapped into suitable vessels and carried to the moulds. In many instances cranes are used to transport the molten metal. Here also the application of hot air has been attended with a great saving of fuel.

Reverberatory Furnace. In some cases pig-iron is melted in a reverberatory furnace, the iron being placed on the smelting-hearth, which is covered with sand; the hearth is slightly inclined and narrowed towards the tapping-hole. A strong coal fire is made up, and the flame playing across the fire-bridge is directed over the entire length of the furnace, and thence into a high chimney. The molten metal on being tapped is conducted to the moulds in the same manner as with the cupola furnace. Rather more than 50 cwts. of pig-iron can be melted at once in a reverberatory furnace; but since the air has free access, the iron becomes gradually decarbonised, and is thus rendered unfit for castings.

Making the Moulds. The most essential, and also most difficult, part of the iron-founder's work is the proper construction of the moulds. According to the materials from which the moulds are constructed, we distinguish—1. Sand moulding or green-sand moulding, the material being a peculiar kind of sand (foundry-sand).—It is necessary for this sand to be exceedingly fine, and yet sufficiently coherent that the sharpest angles and corners will remain standing. This latter property is imparted to the sand by adding as much clay as will render the mass capable of being squeezed with the hand into balls when moistened with water. A certain amount of porosity is also requisite to enable the steam which is formed when the molten iron comes into contact with the mould to readily escape. This property is communicated by the addition of powdered charcoal. Sand-moulds are not dried before the molten iron is poured in. Such objects as plates, grates, railings, and wheels, which are level on one side, are cast in open sand-moulds; that is to say, on the floor of the foundry, previously covered with sand of the requisite quality, the moulds being obtained by pressing the patterns into the sand. For other branches of the work, as, for instance, iron-pots, the box mould is used. 2. Dry sand moulding.—The forms are made in sand and clay, or loam, care being taken to dry the moulds thoroughly before casting. 3. Loam-casting.—The material used for this purpose is loam, which, previous to being used, is sifted, moistened, and mixed with horse-dung to prevent the moulds from cracking during drying. 4. Case-hardening, or casting in iron moulds.—This mode of casting iron only applies to some peculiar descriptions of work, as, for instance, the cylinders of rolling-mills, some kinds of shot and shells, and railway waggon-wheels.* By the use of iron moulds, the casting cools and solidifies very rapidly, and, as a consequence, the outer layer becomes converted into white cast-iron, which is very hard. Thus the cylinders for rolling-mills can be so made, that while the surface is very hard, they are not brittle, and, therefore, fragile, because the interior consists of grey cast-iron.

Fig. 6.

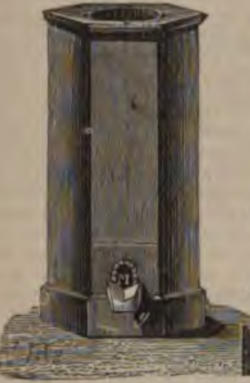
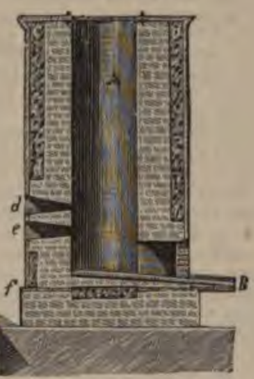


Fig. 7.



Green-sand casting is by far the most general mode of casting: furnace bars, cast-iron railings, grates, plates, wheels, and a variety of objects, are thus made. Dry-sand moulding is used for the casting of iron gas- and water-pipes, and also of cast-iron ordnance. This latter is preferably made from such pig-iron as contains grey and white iron mixed; a higher degree of toughness and elasticity can thus be obtained. Dry-sand moulding is also used for the making of small ornamental objects, so-called *fer de Berlin*, such as cast-iron ink-stands, candlesticks, and a peculiar kind of cast-iron pins, as well as brooches, ear-rings, and similar things. Loam-moulding is used for the casting of large-sized cauldrons, bells, and other large objects for which no wooden pattern is made; also for the casting of steam-engine cylinders. We distinguish in this kind of moulding three chief parts, viz.:—

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* This may be the case in Germany; but in this country the wheels are made of best wrought-iron, and forged by means of steam-hammers.—Ed.

a. The core, or kernel, the size and shape of which corresponds to the interior of the object to be cast.

b. The foundry-pattern.

c. The exterior mould, also termed the case.

The loam mouldings are very rapidly dried; the casting of statues and other monumental work is done by loam moulding, but zinc is beginning to supersede iron for this purpose. Whenever objects have to be cast, the surface of which is very unequal, *i.e.*, so shaped that a partial dismounting of the case is impossible, as may happen for instance with statues and monumental work, the shape is made on the core by means of wax: the pattern maker constructs a pattern, often consisting of a number of loose pieces; into this the molten wax is poured, and the mould thus obtained is carefully placed on the core and properly joined. The wax mould is brushed over with a mixture of pulverised graphite and very finely divided clay, which operation is several times repeated; after this the mould is covered with a layer of loam mixed with cow hair, and as soon as this layer is dry the wax is removed by applying a gentle heat, a channel having been left by which the wax can escape.

Annealing. Tempering. The castings, when sufficiently cool, are cleaned from adhering sand, the seams cut off with a cold chisel, and in many cases submitted to a series of mechanical operations, as, for instance, cast-iron ordnance, which has to be bored, while other objects have to be worked in the lathe and planed. Frequently cast-iron objects have become as hard and brittle as if they had been cast from white pig-iron, and consequently are unfit for filing, &c.; such iron is restored to the requisite softness by annealing or tempering. In this operation the castings are submitted to a strong red heat and cooled slowly, being at the same time protected from the oxidising influence of the air; the annealing is effected either by a physical or chemical process. If the former is used, the castings are simply covered with a thick layer of clay and made red-hot, the effect being a simple rearrangement of the molecules of the iron, which is thus rendered soft again; the heating to redness is also sometimes effected by placing the castings under a layer of dry sand or in suitably constructed vessels filled with charcoal or coke powder. If it is desired to impart to the castings somewhat of the strength and toughness possessed by steel and malleable iron, the tempering is so arranged, and heat applied for a longer time, while the metal is surrounded by a mixture of pulverised charcoal, bone-ash, and forge scales, red oxide of iron, oxide of manganese, or oxide of zinc; cast-iron which has been uniformly and thoroughly decarbonised, is called malleable cast-iron. A great many objects formerly exclusively made of wrought-iron are now cast and treated in this way, while a number of others, inclusive even of razors, are made of cast-iron superficially converted into steel by a method which will be described under the heading of Steel. In order to prevent the rusting of articles made of cast-iron, they are frequently covered with a varnish made from coal tar and powdered graphite, or boiled linseed-oil and lamp-black, and when intended for ornamental or domestic use they are bronzed or burnished.

Enamelling of Cast-Iron. Among the first cast-iron objects ever enamelled were the pans used in kitchens for culinary purposes, but at the present time, especially in England, the enamelling of cast-iron is carried on to a large extent, and includes a variety of things made of cast- and even wrought-iron. The process in use is briefly as follows:—The surface of the cast-iron to be enamelled is first carefully cleaned by scouring with sand and dilute sulphuric acid, next a somewhat thickish magma, made of pulverised quartz, borax, feldspar, kaolin, and water, is brushed over the clean metallic surface as evenly as possible, and immediately after a finely powdered mixture of feldspar, soda, borax, and oxide of tin is dusted over, after which the enamel is burnt in by the heat of a muffle. In France an enamel is applied which consists of a mixture of 130 parts of flint glass, 20½ parts of carbonate of soda, and 12 parts of boracic acid fused together and afterwards ground to a fine powder. Enamelled iron has in some manufactured articles taken the place of tinned iron or zinc.

β. Malleable, Bar, or Wrought-Iron.

Bar Iron. Refined Iron. In comparatively olden times the custom was to produce malleable iron direct from its ores by a process still in use to some extent in Styria, Illyria, Italy, Sweden, some parts of Asia, Andorra, and other localities. The process (a modification of which is known as the Catalan process) consists in the reduction of the iron ores, which must be very rich and pure, by means of charcoal, which serves also as fuel on a hearth, the combustion being aided by a blast, often simply bellows; the lump of iron thus obtained is immediately submitted to the blows of a heavy forge hammer. Excepting in the few instances just mentioned, this process of direct extraction of iron from its ores has been altogether abandoned, and has given place to the production of malleable iron from pig-iron; the process by which this is effected is termed refining. and consists in the removal of the greater portion of the carbon and other impurities contained in the crude metal by oxidation. The crude metal chiefly employed for refining is white pig-iron, preferably that containing the least possible quantity of carbon, because this kind of iron becomes soft before melting and remains for a long time very fluid, and therefore presents a larger surface to oxidising agents; the chemically combined carbon of white pig-iron burns far more readily than the graphite contained in the crude grey cast-iron. The refining process is executed either:—(1) On hearths (the German process); or (2) In reverberatory furnaces (puddling or English process); In the preparation of bar-iron (3) by the forcing of air into the molten metal (Bessemer and other similar processes). This latter process is described under Steel.

German Iron-Refining Process. The hearth on which this process is carried out is represented in Fig. 8. The crude iron is placed in the cavity *a* of the hearth, *b*, and the metal is brought to fusion in such quantity that the molten mass has a length of from 1 to 1·3 metre, a width of about 27 centims., and a thickness of from 4 to 9 centims. The cavity, *a*, is lined with thick plates of iron, and the tuyere, *c*, supplies the necessary air from a blast which is directed against the molten metal. The hearth is first filled with ignited charcoal; next the blast is turned on, and then the crude metal is placed on the hearth, *b*, and becoming gradually melted, flows into the cavity, *a*. The action of the blast causes the combustion of the carbonaceous matter of the metal, while the sand adhering to the pigs, the silica due to the oxidation of the silicium contained in the crude iron, and the silica contained in the ash of the fuel also play an important part in the process, because these substances combine with the protoxide of iron which is present, forming a slag,* composed of basic silicate of protoxide of iron (in 100 parts, 68·84 protoxide and 31·16 silica). This slag protects the iron during the refining process, but is gradually run off, care being taken, however, to leave a sufficient quantity to cover the metal. Mixed with forge scales (a mixture of proto- and peroxide of iron,) the slag of the first refining is employed in the further refining process to decarbonise the iron. When crude cast-iron is heated to redness along with these materials, the oxygen contained in them is given off, and combining with the carbon contained in the cast-iron, forms carbonic oxide and leaves malleable iron. The refining process also causes the more or less complete elimination of such substances as aluminium, phosphorus, and manganese from the crude metal, by converting them into alumina, phosphoric acid, and protoxide of manganese, all of which are taken up in the slag. As soon as all the iron has become fluid the slag is run off and the metal exposed to the

FIG. 8.

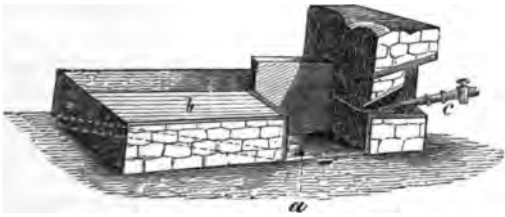
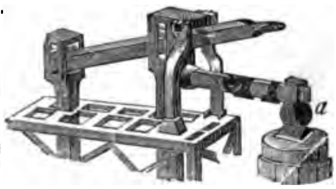


FIG. 9.



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* According to MM. Mitscherlich, Hausmann, Rothe, and others, the slag sometimes assumes the crystalline form and composition of olivine.

action of the blast, care being taken to work the metal about so as to render the action uniform; the somewhat thickish fluid mass becomes during decarbonisation more and more fluid; and the stirring up, or raising up, as the operation is termed, is continued until the iron is refined, which is shown by the fact of the slag becoming very rich in protoxide of iron. Towards the end of the operation, the rich slag, SiO_4,Fe_2, is formed, which along with forge scales, is employed for decarbonising the metal. This rich slag is never crystalline in structure, but exhibits a dense tough mass of higher specific gravity than the raw slag. The operation, called the last breaking up of the lump, consists, first, in the rendering of the entire mass (the contents of the hearth) semi-fluid by increased heat; and, secondly, in the separation of the slag from the metal. This end having been attained, the lump, or ball, or bloom, is removed from the fire, in the red-hot state, and brought under the lift-hammer, *a* (Fig. 9) which is set in motion by means of a lifter and beam. By the blows of the hammer all the particles of slag are squeezed out from the metal; afterwards the lump is cut into smaller pieces, which are forged into bars; 100 parts of crude cast-iron yield on an average 70 to 75 parts of malleable iron.

Swedish Refining Process. The Swedish process of iron-refining (also called Walloon-forging) differs from the German process, inasmuch as only small quantities of crude metal are operated upon at a time, while no slag is added, the decarbonisation being effected by the action of the oxygen of the air. This process requires a great deal of fuel (in Sweden almost exclusively charcoal), while at the same time a not inconsiderable quantity of the iron is oxidised. The malleable iron obtained is, however, of far better quality, being denser and tougher, owing to greater purity and freedom from slag.

The Puddling Process. The process designated by this name is carried on in a reverberatory furnace. In countries where charcoal is scarce, and hence too expensive to be applied to the refining of iron, coal is used, and, indeed, of later years, has become more generally employed on the Continent for this purpose. For, although the iron thus obtained is of inferior quality to that refined with charcoal, to the use of coal alone must the increase in the production of iron to the present enormous extent be attributed. Since coal contains sulphur, direct contact with iron has to be avoided, and the operation is carried on in a reverberatory furnace, which, in **Puddling Furnace.** this instance, is termed a puddling furnace, represented in vertical section in Fig. 10, and in horizontal section in Fig. 11. F is the fire-place, A the puddling hearth, and C the flue along which the gases are carried to the chimney. The puddling-hearth, A, consists of a square iron box, to which air has free access from the fire-place. A layer of refining (puddling) slag, to which some forge-scales have been added, is first placed on the hearth, and heated until it begins to soften at the surface. This point reached, the crude metal (by preference white cast-iron) is placed on the hearth in quantities of from 300 to 350 lbs. at a time and heated. When softened, the iron is spread evenly over the surface of the hearth by means of a rake or stirrer, and continually stirred about (puddled), the heat being greatly increased. D and E represent openings giving access to the hearth for the tools, capable of being readily closed.

The soft pasty mass of metal exhibits on its surface blue flames of burning carbonic oxide, the metal becoming at the same time thicker and thicker: the slag which is formed runs off at B, and is tapped at intervals at *o*. When the iron has been sufficiently puddled, it is scraped together and formed into lumps or balls, which are submitted to the action either of heavy hammers or squeezers, to free the metal from slag. Grey cast-iron, when used for puddling, is first converted into white cast iron by smelting in a reverberatory furnace, known as the refining process.

The theory of the puddling process is the following:—The current of air which comes into contact with the molten iron causes the formation of a not inconsiderable quantity of protoperoxide of iron, the oxygen of which eliminates the carbon contained in the pig-iron in the shape of carbonic oxide, which burns off with a bluish flame. The progress of the decarbonisation renders the mass more and more pasty; while, in the interior, pieces of malleable iron are gradually formed, which, being gathered together by means of the rake, become loosely welded, and the iron not fully decarbonised runs together, and being well stirred up soon undergoes the same change. Although this *résumé* of the puddling process is theoretically correct, in practice the process is not so simple, because—1. It is scarcel possible to mix all the carbon-containing iron intimately with the protoperoxide, and, as consequence, some of that oxide remains mixed with the iron, which is thereby rendere incapable of being welded (the iron loses cohesion and becomes of a gritty nature); thi substance has to be, therefore, removed by the addition of coarse slag, which is thus converted into refined slag. The oxidation of the iron causes a loss of some 4 to 5 per cent. while the loss from the combustion of the carbon amounts to a further 5 per cent. 2. Th crude iron always contains more or less blast-furnace slag and adhering sand and dirt containing silica. During the puddling process any free silica present combines with the blast-furnace slag, and when this slag, rich in silica, comes at the end of the process into contact with protoxide of iron, while carbon is deficient, a portion of the silica (or silicic acid) combines with the oxide, forming a slag which adheres to the sides and bottom of the hearth, while a basic, not easily fusible slag remains mixed up with the metal. In the puddling process the great drawback is that the complete removal of the slag from the iron is practically impossible; at least, such has been the case hitherto. That iron prepared in this way, which may even contain two or more per cent. of such slag, is some times brittle and cold-short is not to be wondered at.

FIG. 10.

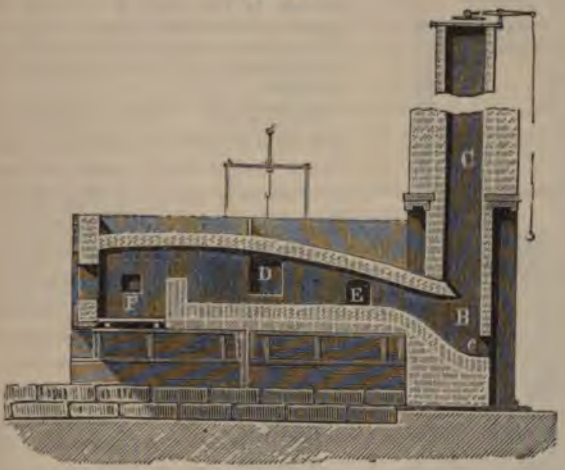
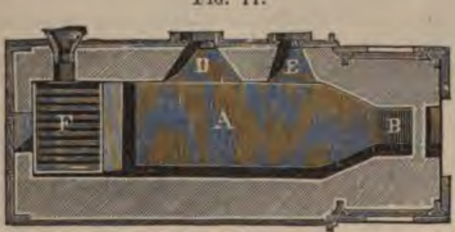


FIG. 11.



Heating with Gases. Instead of employing coal or coke as fuel, the reverberatory furnaces are often heated with combustible gases escaping from the blast-furnaces or with gas made for the purpose in a generator—an arrangement not unlike a coke-oven, in which such refuse fuel as cannot be otherwise utilized, viz., waste of timber-yards, refuse charcoal, peat, and small coal, is submitted to dry distillation. The generator is connected to the reverberatory furnace in such a manner that the gases evolved in the former reach the latter very highly heated. For some years Siemens's regenerator-furnace has been applied to this purpose, and found to surpass all other arrangements of the kind. When crude pig-iron contains much phosphorus, that element may be eliminated during the puddling process by adding to the metal a mixture of manganese, common salt, and clay, reduced to powder. Sulphur, when present, may be burnt off by adding litharge; steam has also been used successfully for this latter purpose.

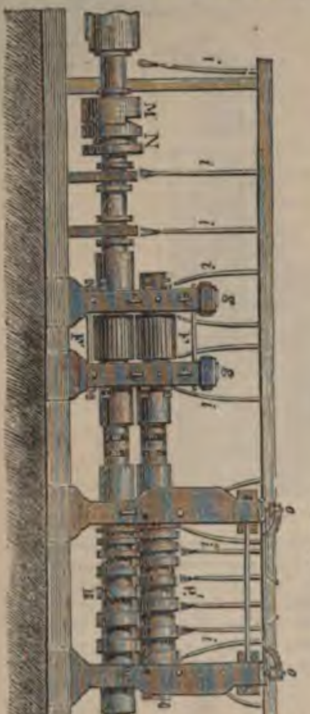


Fig. 12.

Refining of Iron by Mechanical Means.

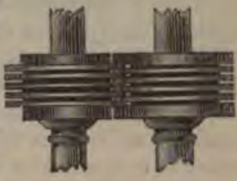
Rolling Mills.

The metal obtained by the puddling process is submitted to heavy hammering or to squeezers in order to remove as much mechanically adhering slag as possible; after this it is ready for the operations carried out in the rolling mill (Fig. 12) which consists in the main of the following parts:—B B' and A A' are grooved rollers made of chilled cast-iron; A A' are destined for shaping flat bars, and B B', for the shaping of square bars; by means of the nuts, *o o*, the position of the rollers towards each other can be regulated: the tubes, *i i*, carry water for keeping cool portions of the machinery. The contrivance M N serves to connect or disconnect the rollers from the steam engine or water- wheel from which is obtained the motive power; the cog-wheels F and *c* impart motion to the cog-wheels F' and *c'* connected with the upper rollers A' and B', which are thus made to move in the opposite direction to the under rollers. The metal to be rolled is first roughly shaped by means of heavy hammers (steam hammers are now often used), and then passed gradually through the variously sized grooves of the rollers. Fig. 13 exhibits rollers of a peculiar construction, viz., steel rings or discs wedged to iron shafting so as to form alternately large and small grooves for the manufacture of thin bars of iron, such as nail-rods, &c.

A variety of rolled iron objects are made; among these, square and flat bars, round bars, T-pieces, angle-iron, hoop-iron, and nail-rods; railroad rails constitute an important item.

Boiler Plate Rolling. The rolling of boiler- and armour plate is an isolated branch, since it requires a metal of good quality, combining softness with toughness, and capable of being worked far below red heat without becoming too brittle or requiring annealing too often; for boiler- and armour-plates the metal is formed into slabs of proper size, which, while nearly white hot, are forced through the rollers. After each succeeding passage of the slab. the rollers are set tighter, the oxide (forge scale) which is formed on the surface of the metal is removed by brushing with wet coarsely-made heather brushes. Thin sheet-iron is rolled out from plate-iron cut into small slabs, which are at first hot, but at a later stage of the operation the rolling is performed cold, the metal having been previously annealed in properly constructed furnaces. Under the headings of Zinc and Tin the galvanising and the tinning of iron are treated of; corrugated iron is made by peculiarly shaped and grooved rollers.

FIG. 13.



Iron Wire Manufacture.

The drawing of iron into wire requires particularly tough and fibrous metal. In former days iron wire was made by drawing thin circular bars, by the aid of tongs, through holes made in steel plates; in the present day iron wire, if stout, is made with rollers, while the thinner wire is made with machinery to be presently described. The rolling-mill for the drawing of iron wire up to a diameter of about $\frac{1}{4}$ of an inch consists of three rollers provided with grooves which correspond to and catch a bar of iron when placed between, the bar being thus squeezed in the grooves; these rollers make 240 revolutions a minute, and since the diameter is 8 inches their circumferential velocity is = 8·37 feet, or in other words 8 feet $4\frac{1}{2}$ inches of wire pass through the rollers in a second of time; thinner wire is obtained by drawing, with the aid of machinery, the stouter kinds of wire through holes made in hard and unchangeable materials, the size of these holes gradually decreasing. For this purpose the previously annealed wire, from $\frac{1}{4}$ to $\frac{1}{16}$th of an inch diameter, is wound on the reel, A (Fig. 14); the end of the wire shaped somewhat to a point is put through the hole made in the draw-plate, B; this hole being of a slightly less diameter than that of the wire, which is next fastened to the hook, *c* (Fig. 15), of the conically-shaped drum, C, which acquires a rotatory motion from the main shaft, D, (Fig. 14), by means of conically-shaped cog-wheels, an arrangement being provided to connect or disconnect the apparatus from the steam-engine, so as to stop or set in motion the wire-drawing machinery without stopping the steam-engine. The shape of the holes in the draw-plate is of the highest importance for the success of the operation, and to obtain perfectly round wire the holes ought to be quite true; if, however, the holes were made perfect cylinders through the entire thickness of the draw-plates the result would be that the wire, instead of suddenly diminishing in size, would break; on that account the holes are bored funnel-shaped. The draw-plate is made of steel, but for very thin wire hard gems properly fastened and pierced are employed. Iron wire has to be repeatedly annealed during the process, and since by this annealing operation, unless carried on with complete exclusion of air, a layer of oxide of iron is formed, the wire requires treatment in what is technically termed a scour bath, composed of dilute sulphuric acid and a certain amount of sulphate of copper; the thin layer of copper deposited on the wire during the immersion in this bath lessens the friction on the wire in passing through the holes. The thinnest iron wire met with in the trade has a diameter of only $\frac{1}{166}$th of an inch, and is known as piano wire. Iron wire is rendered soft by being heated to redness, and is protected from rusting by immersion in a bath of molten zinc, so-called galvanising. The uses to which iron wire is applied are so varied that it is scarcely possible to enumerate them; this is

FIG. 14.

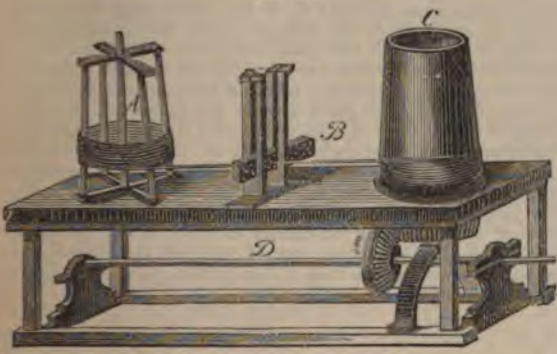
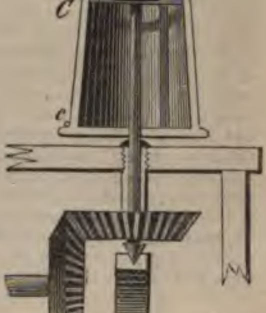


FIG. 15.



the less necessary, as in no country in the world is iron wire so largely used as in the United Kingdom, especially instead of hemp for rope-making.

Properties of Bar Iron. Malleable- or bar iron is made up of an aggregation of fibres which, according to the researches of Dr. Fuchs, are composed of a series of very small crystals. Heavy blows, continuous vibration, and sudden cooling of the metal while red-hot, all cause the particles to lose cohesion and alter the texture from fibrous to granular: a well-known consequence of this change of structure, which is also suddenly induced by great cold, is the loss of tenacity in the iron, often attended with breakage, as happens frequently enough to railway wheel-tyres, axles, &c. The colour of malleable iron is bright grey, the fracture granular or jagged; its specific gravity varies from 7·6 to 7·9 (that of chemically pure iron being 7·844); from 0·24 to 0·84 per cent. of carbon is present in the iron, the greater part in a state of chemical combination, in fact there is only a trace of graphite.

The chemical constitution of malleable iron is shown in the following analytical results:—Sample I. being English iron from South Wales; II., soft iron from Magdesprung on the Harz (Prussia); III., Dannemora iron from Sweden.

	I.	II.	III.
Iron	98·904	98·963	98·775
Carbon	0·411	0·400	0·843
Silicium	0·084	0·014	0·118
Manganese	0·043	0·303	0·054
Copper	*nil*	0·320	0·068
Phosphorus	0·041	*nil*	*nil*

Malleable iron of good quality does not become brittle when placed red-hot into cold water; it ought not to lose its malleability when thus treated: it is far softer than white and bright grey cast-iron, and is therefore easily filed, cut with the cold chisel, planed, and shaped in various ways even cold; it melts with far more difficulty—requiring a much higher temperature—than cast-iron; but malleable iron is possessed of the valuable property of becoming, at a bright red heat (orange heat), so soft as to admit of two pieces being firmly welded together. The malleable-iron of commerce is often more or less mixed with foreign substances which in some cases impair its quality; if sulphur, arsenic, or copper is present, the iron is thereby rendered red-short (breaks when hammered in the red-hot state); silicium renders iron hard and brittle; phosphorus makes it cold-short, *i.e.* rather readily breakable when cold, although not so when red-hot; calcium has the effect of greatly impairing, if not altogether destroying, the welding capability of the metal. As regards the choice of the different qualities of malleable iron for various uses, it is not in the scope of this work to enter into detail, the question being one of applied mechanics and engineering rather than of chemistry. Swedish bar-iron is for certain purposes in high repute, owing to the purity and strength of this kind of iron.

γ. STEEL.

Steel. This substance differs from crude pig-iron and from bar-iron in the amount of carbon it contains; from crude iron, moreover, by being capable of welding; and again from bar-iron by being comparatively readily fusible: in reference to the amount of carbon present, steel holds a position between crude pig-iron and bar-iron. Recent researches have revealed the fact that steel contains nitrogen; but whether this element really contributes to the peculiar properties of steel obtained from different sources is not a definitely settled point. Steel is obtained of various qualities by a number of processes, as will be seen in the following brief reference:—

a. Directly from iron ores:—

1. By the reduction of iron ores directly with the aid of fuel (chiefly charcoal), and a blast on the hearth, the steel being obtained in the form of lumps (so-called natural steel).
2. By the heating of certain iron ores along with coal, but without fusion (cementation steel from ores).
3. By the fusion of the iron ores along with charcoal in crucibles (cast-steel from ores).

b. By the partial decarbonisation of pig-iron (rough steel, furnace-steel, or German steel):—

4. By the refining (partial decarbonisation) of pig-iron by means of charcoal fuel on the hearth (shear-steel).
5. By treating pig-iron in reverberatory furnaces fed by coal or blast-furnace gases as fuel (puddled-steel).
6. By forcing air through molten cast-iron (Bessemer-steel).
7. By heating cast-iron to redness along with substances which will effect decarbonisation below the fusion point of the metal; if the substances employed for partial decarbonisation are iron ores, the steel is called iron ore steel.
8. By melting crude cast-iron with such substances as those just mentioned.
9. By treating crude cast-iron with sodium nitrate (Heaton-steel, Hargreave-steel).

c. By imparting carbon to bar or malleable iron:—

10. By ignition with carbonaceous matter, but without fusion (cementation-steel).
11. By fusion with charcoal (cast-steel).

d. By combination of methods *b* and *c*, as in fluxed steel:—

12. By melting crude pig-iron and malleable iron together.

In India a kind of steel is still made directly from iron ores, and known as wootz (as to the composition of this substance, see the "Chemical News," vol. xxii., p. 46); it is possessed of excellent qualities. The Japanese also understand the art of making steel of most excellent quality by rather rough and primitive means. According to the modes of manufacture, we distinguish the following kinds of steel:—

Rough Steel. This material, obtained by the partial decarbonisation of crude pig-iron, may be either:

1. Rough steel made on a hearth (natural steel), chiefly obtained from the pure spathic iron ore, from which in Styria, Carinthia, Tyrol, and various other parts, porous white pig-iron, or white pig-iron, with granular structure, is first obtained by means of charcoal and coke as fuel; the ordinary grey cast-iron can also be used, but the resulting steel is not of such good quality. The general arrangement of the hearths on which rough steel is made is the same as for the operation of iron refining; the only difference is in the mode of placing the metal in reference to the blast, the operation being so conducted as to cause only the gradual combustion of the carbon; the workmen take care to control the blast and place the metal in a manner which enables them to stop the further action of the air the moment the proper amount of decarbonisation has been effected.

2. Steel obtained in a reverberatory furnace, or puddled steel, obtained from various kinds of cast-iron by a process akin to the puddling of crude cast-iron, the burning off of the carbon not being carried so far. This mode of manufacturing steel is extensively employed, and yields a material well suited for the making of various kinds of machinery, railway carriage-wheel tyres, and is also largely used in the manufacture of cast-steel.

Styrian and Carinthian cast-steel (charcoal iron-steel) is far more expensive than puddled steel, but the former is indispensable—at least on the Continent—for the manufacture of all kinds of cutting-tools.

3. Bessemer-steel. Mr. Henry Bessemer, in 1855, first applied a process of making steel directly from cast-iron; the process consists in forcing large quantities of air through molten crude iron; the consequence is that the conversion of the iron into steel is effected in a comparatively brief space of time; moreover, the resulting steel remains fluid; the difference of the action of the air as an oxidising or decarbonising agent in this instance, as compared with the process of steel-making, mentioned under No. 1 and 2, is that in the case of the Bessemer method, the air thoroughly penetrates and comes into contact with every particle of iron; whereas, in the other instances, the action of the air is only at the surface; and since the steel obtained by methods

1 and 2 is less fusible than the crude iron used, a second refining or smelting becomes necessary to render the steel uniform and homogeneous.

The Bessemer process is executed either in diminutive shaft-ovens or in egg-shaped vessels made of boiler-plate converters, and lined with fire-clay; projecting for some inches through the inside of the bottom, five ⅜th inch wide fire-clay tubes are carried, through which powerfully compressed air can be forced. The apparatus is placed in close proximity to a blast furnace, so as to admit of running the molten iron, purposely kept at a very high degree of heat, readily into the oven or other vessel, while at the bottom of the converter there is an aperture closed with a fire-clay plug, through which the molten steel can be discharged. As soon as the blast is turned on and the vessels half filled with molten iron, a very violent action ensues, the metal apparently begins to boil, flames and myriads of sparks burst forth from the converter (this phenomenon appears to be due to the fact that particles of partly decarbonised iron and a mixture of iron and oxide are driven against each other). According to the duration of the action of the blast (10 to 25 minutes) steel or bar-iron may be made, and of late, even in making steel, the action is carried to the highest possible pitch, and to the resulting metal a portion of molten white pig-iron is added. Bessemer steel is largely used for a variety of purposes; but it is not suitable for the manufacture of such cutting tools and instruments as require a keen and durable edge; on the other hand, Bessemer metal is an excellent material for the manufacture of boiler and armour-plates, ordnance, railroad-rails, and a great variety of heavy machinery. As might be expected, this method of steel-making has rapidly spread from England to all parts of Europe and to America; and as a proof of the handsome profit earned by the inventor, whose royalty amounts to 1s. per cwt., we may state that the total quantity of Bessemer steel produced in Europe in the year 1869 amounted to 5·5 millions of cwts., 70 per cent. thereof being produced in Great Britain.

4. Uchatius and Martin Steel are also directly prepared from crude cast-iron, by mixing granulated crude pig-iron, made from native magnetic iron ore, along with pulverised spathic iron ore, and fusing this mixture in plumbago crucibles. M. Martin replaced the use of the crucibles in this process by that of the somewhat hollow floor of a reverberatory furnace heated by means of a Siemens's regenerative gas-furnace. A quantity of crude pig-iron is melted under a layer of slag, and from time to time bar-iron is added until a sample taken out is found to possess the texture and good qualities of malleable-iron. When this stage has been reached, a certain amount of crude cast-iron is added, whereby the entire quantity of metal is converted into a kind of cast-steel, chiefly suited to the making of railroad-rails, wheel-tyres, and especially gun-barrels and ordnance. Tunner's steel, which dates from 1855, also known as malleable cast-iron, is obtained by igniting white pig-iron to bright redness with substances which give off oxygen (oxides of iron and zinc and peroxides of manganese) when thus treated.

5. Heaton steel. Prepared by a process devised by Mr. Heaton, in which crude iron is heated with nitrate of soda (Chili-saltpetre). By this method not only the carbon is eliminated, but the sulphur and phosphorus being oxidised and converted into phosphates and sulphates, find their way into the slag. The principle of this method is the same as in Mr. Hargreaves's plan, and again identical with a proposed new method of Bessemer steel-making.

Steel Making by Imparting Carbon to Wrought-Iron.

II. The second kind of steel is that known as cementation-steel—a metal prepared by the ignition of bar-iron in contact with carbonaceous matter, preferably containing nitrogen. The bar-iron to be employed for this purpose should be of the very best quality, and since in Great Britain and France, the best iron produced is not good enough, both these countries draw largely upon Sweden for a supply of Dannemora iron, made from magnetic and red hæmatite-iron ores mixed. The Russian iron from the Ural is of the same good quality, but the transport is at present far too costly. It is almost superfluous to mention that the chief seat of the steel manufacture in England is Sheffield.

The process of making cementation-steel is simple enough. The bars of iron are placed in fire-clay boxes, in layers alternating with the carbonaceous matter (cementation-powder). Two of such boxes are placed in a furnace which is heated with coal, and the boxes are kept at a red heat for some six or seven days, and after cooling, the bars, converted into steel, are taken out. Each furnace contains from 300 to 350 cwts. of iron. In the cementation-powder such substances as will form cyanide of potassium, or ready-formed cyanides, ought to be present. It appears from recent researches that cyanogen (CN) is to be viewed as the carrier of the carbon to the metal. The crude steel (blistered-steel) obtained by this operation is not, as such, fit for use, but has to undergo a process of purifying.

Refined-Steel. Shear-Steel. Not only cementation-steel, but also that obtained by the other methods, is too coarse and not sufficiently homogeneous for immediate use, and therefore a process of refining has to be resorted to. This process consists, firstly, in the hammering out of the steel bars, previously made red-hot, into thin rods, which are, while red-hot, quenched with cold water. Next a number of these are placed together in the form of a bundle, which is again made red-hot, well hammered, and afterwards rolled into bars. The method of refining here alluded to is more suited to the quality of steel obtained from crude pig-iron than to cementation-steel. Steel thus refined, on account of being used for making large pairs of scissors or shears, bears the name of shear-steel.

Cast-Steel. Cast-steel, in modern industry, has assumed a most enormous importance, as evidenced by such gigantic works as those of M. Krupp, at Essen (Prussia). The existence of these works notwithstanding, Sheffield takes the foremost rank in the manufacture of cast-steel. The following is the plan pursued:—The bars of blistered-steel, cut to a convenient size, are introduced into crucibles made of Stourbridge clay, which are heated in furnaces similar to glass-melting ovens, fed with coke or coal as fuel; the molten metal is cast into bar-shaped moulds, and the bars are, after cooling, again heated to redness and hammered or rolled out in a mill. As to the uses to which cast-steel is applied, suffice it to say that heavy ordnance, as well as large bells, excellent cutting-tools and files, best cutlery, and many surgical instruments, number among them. Cast-steel is homogeneous, and therefore strong and durable.

Steel made from Malleable and Crude Cast-Iron. III. A third kind of steel (varying according to the mode and materials of production) is that called Glicenti-steel, obtained by melting together a peculiar white pig-iron (spiegel-iron), and bar or malleable-iron. The toughness, hardness, and malleability of this metal depend upon the quantity of bar-iron which has been added to the mixture.

Surface Steel-Hardening. It frequently happens that for certain purposes soft iron only requires to be converted into steel superficially, an operation termed surface-hardening or surface-steel hardening, which is done by placing the metal, previously polished with emery, in a suitable vessel covered in cementation-powder (see above); the vessel and contents being next heated to redness, malleable iron tools, spanners, for instance, keys, and small objects, may be readily surface-hardened by being, while red-hot, dusted over with powdered ferrocyanide of potassium, yellow prussiate, or with pulverised borax and pipe-clay.

Properties of Steel. The colour of steel is bright greyish-white, its texture is uniformly granular, the better the quality the smaller the grain. Sound soft (that is not hardened) steel, never exhibits the coarse texture characteristic of crude cast-iron, nor the fibrous texture of bar-iron. Hardened-steel exhibits a fracture very similar to that of the finest silver, so close that the granular texture can hardly be detected with the naked eye. When red-hot, steel is nearly as readily malleable as bar-iron, and may be welded, but very careful management is required to prevent its becoming decarbonised. By immersing a piece of steel in dilute hydrochloric or nitric acid, the texture of the metal becomes apparent, and this test may be applied to determine the quality The specific gravity of steel varies from 7·62 to 7·81, and decreases in hardening (for instance, from 7·92 to 7·55); the quantity of carbon contained in steel varies from 0·6 to 1·9 per cent; the toughness, tenacity, and hardness of steel, increase with the quantity of carbon it contains, but good steel never contains graphite; the high degree of elasticity exhibited by good steel decreases with the hardness. When red-hot steel is suddenly quenched with cold water, the metal becomes far harder, but also brittle, and will even scratch glass and withstand the file; when brightly polished, if steel is gradually heated, it assumes peculiar shades of colour (annealing or tempering colour). This colouration is due to the formation on the surface of the steel of thin layers of oxide, which exhibit colours like other very thin surfaces—soap bubbles, for instance, or a drop of oily or tarry matter extended over water. The operation which causes the formation upon steel of these colours is called tempering.

Tempering.

In judging the proper temperature and the corresponding hardness these tints serve admirably. Since it is often rather difficult to heat a piece of steel uniformly, molten metallic mixtures are employed, being chiefly made up of tin and lead; the bright hardened steel is kept in these molten mixtures until it has assumed the temperature of the bath. The following tabulated form exhibits the composition of the metallic baths, which experience has proved to be the best for the tempering of cutlery:—

	Composition of metallic mixture.		Melting point.	Temperature.
	Pb.	Sn.		
Lancets	7	4	220°	Hardly pale yellow.
Razors	8	4	228°	Pale-yellow to straw-yellow.
Pen-knives	8½	4	232°	Straw-yellow.
Pairs of scissors	14	4	254°	Brown.
Clasp-knives, joiners' and carpenters' tools	19	4	265°	Purplish-coloured.
Swords, cutlasses, watch-springs	48	4	288°	Bright-blue.
Stilettos, boring-tools, and fine saws	50	2	292°	Deep blue.
Ordinary saws	in boiling linseed-oil		316°	Blackish blue.

Such tools as are required to work iron and other metals and hard stones are heated to bright-yellow; razors, surgical-instruments, coining dies, engravers'-tools, and wire-drawing plates follow next to straw-yellow; carpenters'-tools to purplish-red; while such tools and objects as are required to be elastic are heated to the violet or deep-blue tint; the less steel is heated the harder it remains, but also the more brittle. Other substances than carbon (for instance, silicon and boron) may be capable of imparting to iron properties similar to those we are acquainted with in steel. Some other metals mixed with steel in greater or lesser quantity improve the quality in some respects; for instance, for the last few years steel has been made in Styria, which, owing to its containing tungsten, is exceedingly tough and hard.

Steel and other Metals.

Damascene, or Wootz Steel.

This steel, specially celebrated for making swords, was first made at Damascus. Its name, Damascene, is applied to the property it possesses of exhibiting a peculiar appearance when acted upon by an acid; but this appears to be due rather to some imperfection of the welding of the metal, since, after melting, the same peculiar shades of colour do not appear. We have already alluded to the recent researches concerning the true composition of this metal. One of the largest collections of tools, swords, gun-barrels, and bars of this kind of steel to be found in Europe is in the India Museum, Whitehall. In order to elucidate the composition of some kinds of steel, the following analyses are appended:—The samples are—1. Refined steel, from Siegen (Prussia); 2. Cast-steel, from Schmalkalden (Prussia); 3. Puddled-steel; 4. Steel from Russian cast-ordnance; 5. Cementation-steel, Elberfeld (Prussia); 6. English cementation-steel; 7. Krupp's steel (Essen).

		1.	2.	3.	4.	5.	6.	7.
Iron		97·91	98·154	98·602	98·75	99·01	99·12	99·351
Carbon	C	1·69	1·730	1·380	1·02	0·41	1·87	0·532
	Cβ		0·010	trace	0·15	0·08		
Silicium		0·03	0·202	0·006	0·04	—	0·10	0·032
Sulphur		trace	0·003	—	—	—	—	0·001
Phosphorus.. ..		—	—	trace	—	—	—	0·001
Manganese.. ..		—	—	0·012	—	—	—	—
Copper..		0·37	—	—	—	—	—	—
		100·00	100·000	100·000	100·00	99·50	101·09	99·917

Siderography or Steel Engraving. The engraving of steel requires plates made of cast-steel, which, in order to be sufficiently soft for the engraver's tools, are first superficially decarbonised, and after the engraving is made, again hardened. The engraved plate is not employed direct for printing, but is used as a matrix for the preparation of plates to be printed from; this process is carried out in the following manner:—A solid cast-steel cylinder, turned in a lathe, is superficially softened, and the engraved plate is placed under this cylinder, so that with great pressure and a slow revolution of the cylinder, the plate moving also very slowly, a *relief* of the engraving is produced on the cylinder, and this being again hardened, is employed to reproduce the engraving on other metallic plates, which may be either copper or soft steel. Instead of engraving the design on soft steel plates, etching is often resorted to, for which purpose corroding fluids, such as nitric acid (aquafortis), nitrate of silver, sulphate of copper in solution, or, lastly, a solution of 2 parts of iodine, 5 of iodide of potassium, and 40 of water, are used.

Statistics of Steel Production. The annual production of steel in Europe may be roughly estimated for 1870 at 6,285,000 cwts. at 50 kilos. to the cwt.

The imperial English cwt. is equal to 508·023 kilos.; of this total the undermentioned countries produce:—

United Kingdom of Great Britain and Ireland	2,300,000
France	1,350,000
Belgium..	125,000
North German Confederation	1,120,000
Austria	900,000
Sweden	250,000
Russia	150,000
Italy	75,000
Spain	15,000
Total	6,285,000

IRON PREPARATIONS.

Copperas, Green Vitriol. The substance called copperas and green vitriol, sulphate of protoxide of iron ($FeSO_4+7H_2O$), is met with in the trade in the form of greenish-coloured crystals possessed of an inky astringent taste; on exposure to dry air the crystals effloresce, and are gradually converted into a yellowish powder—basic sulphate of peroxide of iron. 100 parts of the chemically pure crystallised salt consist of:—

26·10	parts of	protoxide of iron.
29·90	,,	sulphuric acid.
44·00	,,	water.

Preparation of Green Vitriol as a by-product in Alum Works. Since the minerals ordinarily used in the manufacture of alum—the alum schists—generally contain iron pyrites (FeS_2), either as such or already partly converted into a basic sulphate of the peroxide (which, on being treated along with the alum shale, becomes by weathering and roasting converted into protosulphate and peroxide of iron), green vitriol is frequently a by-product of alum manufacture, and is obtained by evaporating the mother-liquor containing iron, and leaving it to crystallise. In some localities, as, for instance, at Goslar (Prussia), on the Hartz mountains, the liquor obtained by the lixiviation of the iron-containing minerals alluded to is first evaporated for the separation of the green vitriol, then a potassa or ammonia salt added to the remaining acid liquid to obtain alum.

Preparation of Green Vitriol in Beds. The material sometimes rather largely found in coal pits, and called brass (iron pyrites), is collected and placed in layers over a somewhat excavated surface, which has been rendered impervious to water by puddling with clay, and made to incline slightly in one direction where water-tanks stand, into which scraps of old iron are placed with the view of saturating any free acid; the pyrites, placed on these beds to a thickness varying from 1½ to 3½ or 4 feet, is slowly oxidised by atmospheric agency, and the falling rain carries into the tanks a more or less strong solution of copperas, which, when sufficiently concentrated, is slowly evaporated, some scrap iron being placed in the evaporating-pans. **Green Vitriol from the residues of Pyrites Distillation.** In countries where iron pyrites abounds, and fuel and labour are sufficiently cheap to make the distillation of sulphur from pyrites a profitable business, the residues are utilised in green vitriol making, a salt which thus made must, of necessity, contain a good deal of impurity. **Green Vitriol from Metallic Iron and Sulphuric Acid.** The brown sulphuric acid or chamber acid, also such waste sulphuric acid liquids as are obtained in the oil and petroleum refining, are sometimes used as solvents for scrap-iron for the preparation of green vitriol, which may also be made by boiling the finely pulverised puddling and iron refining slags with sulphuric acid.

From Spathic Iron Ore. In localities where spathic iron (carbonate of protoxide of iron, $FeCO_3$) occurs in a pure state, that mineral may be usefully applied to the preparation of green vitriol by treatment with sulphuric acid, and evaporating the solution thus obtained. The sulphate of iron (protoxide), prepared on the large scale, is often met with crystallised round a small thin stick of wood, which is hung up in the solution to promote crystallisation; sometimes, at least abroad, a so-called black vitriol is met with, which is simply green copperas superficially coloured black by means of some astringent decoction, such as nut galls.

Uses of Green Vitriol. This substance is employed as a disinfectant, as a mordant in dyeing and calico printing for various black and brown shades, for the preparation of ink, the deoxidation of indigo—so-called cold vat—in gas purifying, in the precipitation of gold from its solutions, in the preparation of Prussian blue, in the manufacture of fuming (Nordhausen) sulphuric acid, and for a host of other purposes.

Iron Minium. During the last 10 or 15 years a large number of substances under this name have been introduced as paints, especially for iron sea-going vessels and other ironwork. The late Dr. Bleekrode analysed two samples of this paint, one of which, made and sold by M. Cartier in Belgium, was found to consist in 100 parts of:—

Moisture	2·75
Red peroxide of iron	68·27
Clay	27·60
Lime..	0·40

A sample of Holland's iron minium was found to contain in 100 parts:—

Water	6·00
Peroxide of iron ..	85·57
Clay (burnt)	8·43

In Dr. G. J. Mulder's work on the "Chemistry of Drying Oils"*—second or applied part—attention is called to the fact, and supported by results of analyses of different iron miniums obtained by the author, that some of these paints contain free sulphuric acid, which is always present in colcothar; this acid may exercise an injurious effect on iron painted with such materials.

It is hardly necessary to point out that the use of iron minium as paint is less expensive than the use of red-lead, in the proportion of 20 to 30 for coating the same extent of surface.

Yellow Prussiate of Potassa.

The yellow-coloured salt, generally known as yellow prussiate of potassa (ferrocyanide of potassium, $K_4FeCy_6 + 3H_2O$), is, in a technical point of view, a very important substance. It crystallises in large lemon-coloured prismatic crystals, which are not affected by exposure to air, are not poisonous, and possess a sweetish bitter taste. This salt is soluble in 4 parts of cold and 2 of boiling water, but is insoluble in alcohol; in 100 parts there are:—

37·03 Potassium,
17·04 Carbon, } Cyanogen,
19·89 Nitrogen, }
13·25 Iron,
12·79 Water.

At 100° the water is driven off. The salt is prepared on a large scale by igniting such carbon as contains nitrogen to a red heat with potassa-carbonate in closed vessels. The quantities of the materials may be varied, the relative proportions being given by some makers as 100 parts of potassa-carbonate to 75 of the nitrogenous carbon, or, according to Runge, 100 parts of carbonate of potassa, 400 of calcined horn, and 10 parts of iron-filings.

The fusion of these ingredients is carried on either in closed iron vessels of a peculiar shape, or in a reverberatory furnace. The iron-vessel, *a*, termed a muffle (Fig. 16) is egg or pear-shaped, having a diameter of 1·2 metres, a width of 0·8 metre, and varying from 12 to 15 centims. in thickness. As shown in the woodcut, the iron vessel is placed in the furnace in such a manner as to be exposed to the action of the flame and hot gases on all sides, being supported at the back by a projection about 27 centims. long, and resting at *g* on the brickwork, leaving space sufficient for the gases generated in the interior to pass off by *c* into the chimney-flues; *m* is an iron cover which is closed during the operation of melting, *g* being an opening in the front wall of the furnace, through which the ingredients are put into the iron vessel, and the

FIG. 16.

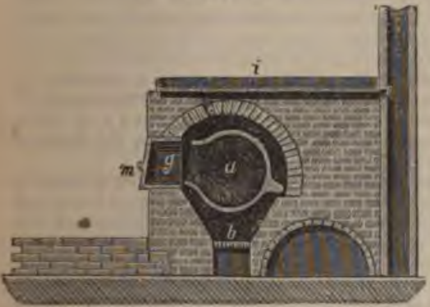
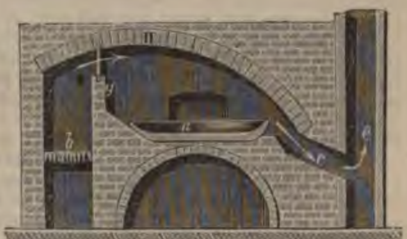


FIG. 17.



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* The original is in Dutch, and the work has not been translated into any other language.

molten mass taken out. The shallow pan, *i*, on the top of the furnace, is intended for the evaporation of the liquor obtained by treating the molten mass with water. The use of the iron vessel, however, is attended with the serious drawback that the iron is eaten into holes in a comparatively short space of time; and, though this action is greatest on the lower part of the vessel, and it may therefore be turned bottom upwards, and the holes stopped with fire-clay, the vessel has soon to be replaced by another. It is on this account, and also owing to the fact that a larger quantity of raw material can be operated upon at once, that instead of the apparatus described above, there has come into general use a reverberatory furnace, Fig. 17, arranged with a shallow cast-iron pan, *a*, from 1 to 1·8 metre in diameter, with a rim about 1 decim. high; *b* is the fire-place; *g* the bridge; *c* a flue leading to the chimney, *e*. Sometimes the hot air is applied to the heating of evaporating-pans, being carried under them before entering the chimney. The result of the ignition is the formation of a black mass, technically called *the metal*, yielding the liquor from which the crude salt crystallises. The salt is purified by re-crystallisation, while the black residue is employed as a manure.

The theory of the formation of the ferrocyanide of potassium is as follows:—The carbonate and sulphate of potassa, the nitrogenous coal and the iron reacting upon each other, give rise to the formation first of sulphuret of potassium, which in its turn converts the iron into sulphuret, while the nitrogen contained in the charcoal unites, under the influence of potassium, with the cyanogen of the carbon, which again in its turn combines with the potassium, giving rise to the formation of cyanide of potassium. When the fused mass is treated with water, cyanide of potassium and sulphuret of iron decompose each other, the result being the formation of ferrocyanide and sulphide of potassium, the last-named salt remaining in the mother-liquor. M. E. Meyer states (1868) that it is more advantageous to employ, instead of the sulphuret of iron, the carbonate of that metal, for the purpose of converting cyanogen into ferrocyanogen, because the ferrocyanide of potassium crystallises far more completely and freely from solutions not containing any sulphuret of potassium. Professor Dr. von Liebig has since proved that the fused mass only contains cyanide of potassium and metallic iron, and not any ferrocyanide of potassium, which is only formed by treating the molten mass with water, or more slowly by its exposure to moist air. Among the materials frequently added to the fusing mass are—scraps of metal, the refuse of leather, dried blood and other dry animal offal, because the ammonia evolved by their decomposition in the presence of an alkali aids the formation of cyanide of potassium. According to M. P. Havrez, the crude suint obtained from wool is an excellent material for the preparation of ferrocyanide of potassium, since 100 kilos. of the suint contain about 40 kilos. of carbonate of potassa, from 1 to 2 kilos. of cyanide of potassium, and about 50 kilos. of combustible hydrocarbons, the heating value of which is at least equal to that of 40 kilos. of coal.

It has been tried to obtain the cyanide of potassium on a large scale, by causing a current of ammoniacal gas to pass through and over carbonate of potassa heated to redness; and also to obtain cyanide of potassium from, or by aid of, the nitrogen of the atmosphere. This process was tried nearly 40 years ago at Mr. Bramwell's works near Newcastle-on-Tyne, but was found to be a failure commercially. The reader interested in a detailed account of this process may find it in the excellently-written chapter on the manufacture of the prussiates, in Richardson and Watts's "Chemical Technology." As it has been proved by experiment that baryta, far more readily than potassa, converts carbon and nitrogen into cyanogen, forming cyanide of barium at a lower temperature, baryta might perhaps be substituted for potassa, but as yet this plan is not carried out commercially. According to Gélis (1861), the yellow prussiate may be prepared by the mutual reaction of sulphide of carbon and sulphide of ammonium, the resulting sulphocarbonate being converted into sulphocyanide of potassium by means of sulphuret of potassium, by which reaction sulphuret of ammonium and sulphuretted hydrogen are volatilised. The sulphocyanide of potassium is next converted into ferrocyanide of potassium by being heated with metallic iron to redness, sulphuret of iron being at the same time formed. It is evident that this process could not be carried out commercially. Mr. H. Fleck described, in 1863, a plan for preparing the ferrocyanide by the action of a mixture of sulphate of ammonia, sulphur, and carbon, upon fusing sulphide of potassium, which thus becomes sulphocyanide of potassium, one-half of the nitrogen of the sulphate of ammonia remaining in the fused metal as cyanogen, while the other half escapes as sulphide of ammonium, which is again converted into sulphate of ammonia. The sulphocyanide of potassium produced is treated with metallic iron at a red-heat, and thus cyanide of potassium and sulphide of iron are produced. This process is also too cumbrous and expensive on a large scale.

Applications of the Yellow Prussiate. This salt is employed in the manufacture of the red-cyanide or prussiate, in the preparation of Berlin blue, and of cyanide of potassium (the impure salt as met with in commerce), in dyeing and calico-printing for the production of blue and brown-red colours, for the purpose of surface-hardening small iron articles, and lastly as an ingredient of white gunpowder, and for use in chemical laboratories.

Red Prussiate. The so-called red prussiate of potassa, properly ferricyanide of potassium, or Gmelin's salt, K_3FeCy, is prepared on a large scale and extensively used in dyeing and calico-printing. This salt crystallises in prismatically-shaped ruby-red-coloured, anhydrous crystals, which consist in 100 parts of:—

$$\begin{array}{l}35\cdot58\text{ Potassium,}\\ \left.\begin{array}{l}21\cdot63\text{ Carbon,}\\ 25\cdot54\text{ Nitrogen,}\end{array}\right\}\text{Cyanogen,}\\ 17\cdot29\text{ Iron.}\end{array}$$

It is prepared by submitting either the solution of the yellow prussiate or that salt in powder to the action of chlorine gas until a sample, when heated, yields no precipitate with a solution of a per-salt of iron. When the dry and pulverised yellow prussiate is acted upon by chlorine gas, the salt is frequently placed in casks, closed so as only to leave a small outlet, while the vessel can be made, by means of machinery, to turn slowly on its axis, so as to bring all the particles of the salt into contact with the chlorine. Sometimes, again, the pulverised yellow prussiate is placed on trays in a chamber, into the top of which chlorine gas is admitted; when no more chlorine is absorbed the newly-formed salt is, if a solution of the yellow prussiate has been operated upon, evaporated to dryness, or in the case where the dry powder of the salt has been taken, the newly-formed salt is dissolved in the smallest possible quantity of water, and the solution left to crystallise, the mother-liquor containing chloride of potassium. This reaction is represented by—

$$\underbrace{K_4FeCy_6}_{\text{Yellow prussiate.}} + Cl = KCl + \underbrace{K_3FeCy.}_{\text{Red prussiate.}}$$

The powdered red prussiate is of an orange-yellow colour. According to M. E. Reichardt (1869) bromine may be successfully employed instead of chlorine for the preparation of this salt, which is chiefly used for dyeing wollen fabrics blue, and, with solutions of caustic soda or potassa, for the Mercerising process of cotton.

Cyanide of Potassium. This salt is obtained in an impure state—Liebig's or crude cyanide of potassium—by the fusion of the yellow prussiate of potassa in a porcelain crucible, continued as long as nitrogen escapes. Carburet of iron sinks to the bottom of the crucible, while the crude cyanide is poured off in a state of fusion; 10 parts of the yellow prussiate of potassium yield 7 parts of crude cyanide, ($K_4FeCy_6 = 4KCy + FeC_2 + 2N$). According to Liebig's plan, the cyanide of potassium is prepared by fusing 1 molecule of ferrocyanide of potassium with 1 molecule of carbonate of potassa; by this method 10 parts of the ferrocyanide, yielding 8·8 cyanide of potassium, mixed with 2·2 parts cyanite of potassa. For all technical and industrial purposes it is far cheaper to use cyansalt, a mixture of the cyanides of potassium and sodium, prepared by fusing together 8 parts of previously dried (anhydrous) ferrocyanide of potassium and 2 parts of carbonate of soda. As this mixture fuses readily, the carburet of iron easily separates; moreover, the salt thus obtained is less liable to decomposition on exposure to air, and its preparation requires less heat. The industrial applications of the crude cyanide of potassium, or of the cyansalt, are the following:—In the process of electro-gilding, for the preparation of *Grénat soluble*, isopurpurate of potassa, from picric acid, and in the reduction of metals. It has been mentioned, while treating of the blast-furnace process, that cyanide of potassium is formed during the reduction of iron.

Berlin-Blue. This substance, so named when it was accidentally discovered at Berlin, in 1710, by Diesbach, is chemically a ferrocyanide of iron, more correctly ferrous-ferric cyanide. A distinct variety of this substance is known as Paris-blue. Three different kinds of Berlin-blue are known, viz., neutral, basic, and a mixture of the two, differing in composition and prepared by different processes.

(*a*). Neutral Berlin-blue, also known as Paris-blue, is obtained by pouring a solution of yellow prussiate into a solution of chloride of iron, or into a solution of a peroxide salt of iron; the result is the formation of a large quantity of a magnificently blue-coloured precipitate, very difficult to wash out and always retaining a certain quantity of the yellow prussiate, which cannot be removed by washing.

(*b*). Basic Berlin-blue is obtained by precipitating a solution of yellow prussiate with a solution of a salt of protoxide of iron (green copperas), the result being at first the formation of a white precipitate of protocyanide of iron, which, either by exposure to air, or by the action of oxidising substances, becomes blue; because a portion of the iron is oxidised and another portion takes up the cyanogen thus liberated, converting some of the protocyanide into percyanide, which in its turn combines with the unattacked protocyanide to form Berlin-blue, with which, however, some peroxide of iron remains mixed. It is stated that basic Berlin-blue is distinguished from neutral Berlin-blue by being soluble in water; but this solubility is due to the presence of some of the yellow prussiate, and is not a property inherent in the basic Berlin-blue in a pure state.

(*c*). As the materials employed on a large scale are neither pure protoxide nor pure peroxide salts of iron, but a peroxide containing protosalt of iron, the precipitate obtained consists at first of a mixture of neutral Berlin-blue with more or less of the white protocyanide of iron, which afterwards becomes basic Berlin-blue; accordingly the Berlin-blue of commerce is a variable mixture of neutral and basic Berlin-blues. The iron salt employed is green copperas (sulphate of protoxide of iron), which of course should not contain any appreciable amount of copper, the salts of this metal, as is well known, yielding with yellow prussiate of potassa a chocolate-brown coloured precipitate.

Old Method of Preparing Prussian-Blue. The sulphate of iron and alum are dissolved together in boiling rain or river-water; the fluid, while yet hot, is decanted from any sediment and forthwith poured into a hot aqueous solution of yellow prussiate, care being taken to stir the mixture, and to add the copperas and alum-solution as long as any precipitate is formed. The liquor is run off, and the precipitate washed with fresh water, until all the sulphate of potassa is removed; after which the precipitate is drained on filters made of coarse canvas. This having been accomplished the substance is suspended in water in a boiler, and, while being heated to the boiling-point, nitric acid is added; after a few minutes' boiling, the contents of the boiler are poured into a large wooden tub or cask, and strong sulphuric acid is added. The solution is now allowed to stand for some time, during which the blue colour fully developes. The Berlin-blue is then thoroughly washed with water, drained on coarse canvas filters, next dried, pressed, and cut into cakes; finally it is dried in rooms heated to 80°. As Berlin-blue, when once quite dry, is reduced to powder with great difficulty, and cannot be brought to the state of fine division as when first precipitated, it is also sent into the market in the state of paste. The alumina derived from the alum is so intimately mixed with the blue that the bulk of the mass is thereby increased without any very perceptible decrease in the intensity of the colour. If the quantity of alumina is very much increased, the colour, of course, becomes much lighter, and this variety of Berlin-blue is then known as mineral-blue; a name also given to a preparation of copper obtained either from the native hydrated carbonate of copper, or artificially prepared by precipitating nitrate or chloride of copper by means of lime and chalk.

Recent Methods of Preparing Berlin-Blue. Among the improvements made more recently, we may briefly notice the following:—1. The mixing of the solutions of copperas and alum with that of yellow prussiate is effected as above described, but great care is taken to prevent any oxidation of the white precipitate, which is converted into an intense blue by being treated with nitro-hydrochloric acid, the chlorine evolved serving as an oxidising agent. The remaining operations, viz., washing, drying, &c., are performed as in the former methods. 2. Perchloride of iron solution is employed for the purpose of converting the white precipitate into blue, while the protochloride of iron thus formed serves at a subsequent operation instead of protosulphate of iron. 3. In some cases perchloride of manganese (Mn_2Cl_6), is applied; likewise a solution of chromic acid, a mixture of bichromate of potassa and sulphuric acid; but it is self-evident that the application of any of these improvements is dependent as regards success in a commercial point of view, upon local conditions, and upon the possibility of advantageously obtaining the various ingredients.

Turnbull's-Blue. By mixing together a solution of red prussiate and of protosulphate of iron in such proportions as to prevent the entire saturation of the former salt, there is obtained a blue-coloured precipitate known in commerce as Turnbull's-blue, consisting of $Fe_2Cy_3,3FeCy$, but also containing some chemically-combined yellow prussiate. MM. Mallett and Gautier-Bouchard have proved experimentally that Berlin-blue may be obtained as a by-product of coal-gas manufacture from the ammoniacal liquor from the spent lime of the purifiers, and from Laming's purifying mixture. The spent lime contains, in addition to the cyanides of calcium and ammonium, a good deal of free ammonia, mechanically absorbed in the moist lime. Free ammonia is first removed by forcing steam through the lime, and collecting the ammoniacal gas in dilute sulphuric acid. The lime is next washed with water, and the liquor obtained, containing the cyanogen compounds, is employed for the manufacture of Berlin-blue. According to M. Krafft's experiments, 1000 kilos. of spent gas-lime yield, when treated as described, from 12 to 15 kilos. of Berlin-blue, and from 15 to 20 kilos. of sulphate of ammonia. Mr. Phipson states that 1 ton of Newcastle gas-coal yields a quantity of cyanogen which corresponds to from 5 to 8 lbs. of Berlin-blue. The manufacture of animal-charcoal also yields, if desired, Berlin-blue as a by-product.

Berlin-Blue as a By-Product of the Manufacture of Coal-Gas and Animal Charcoal.

Soluble Berlin-Blue. As ordinary Berlin-blue is quite insoluble in water, and the basic variety only soluble in the presence of ferrocyanide of potassium, these pigments are only fit for use as paints, and the discovery of the solubility of pure Berlin-blue in oxalic acid is of some importance, for thereby its application as a water-colour becomes possible. This soluble blue is obtained by digesting the Berlin-blue of commerce for 1 to 2 days, with either strong hydrochloric acid or with strong sulphuric acid, which latter, after having been mixed with the Berlin-blue previously pulverised, is diluted with its own bulk of water. The acid is next decanted from the sediment of blue, and the latter thoroughly washed and dried, and then dissolved in oxalic acid, the best proportions being 8 parts of Berlin-blue, treated as just mentioned, 1 part of oxalic acid, and 256 of water. According to other directions, Berlin-blue readily soluble in water can be obtained:—1. By the precipitation of protoiodide of iron with yellow prussiate of potassa, care being taken to keep the latter in excess. 2. By mixing a solution of perchloride of iron in alcoholic ether (*tinctura ferrichlorati æthcrea*, Ph. Russ.) with an aqueous solution of yellow prussiate.

Pure Berlin-blue is of a very deep blue colour, with a cupreous gloss; it is insoluble in water and alcohol, is decomposed by alkalies, concentrated acids, and by heat. The lighter and more spongy it is, the better is its quality; it is employed as a pigment and in dyeing and calico-printing, but in the two latter instances, pigment-printing excepted, it is obtained on the tissues by a circuitous process. The Berlin-blue of commerce is frequently adulterated with alumina, pipe-clay, kaolin, magnesia, heavy-spar, and, according to Pohl, even with starch-paste coloured blue by means of tincture of iodine.

COBALT.

(Co = 59; Sp. gr. = 8·7).

Metallic Cobalt. This metal is found native as cobalt-speiss ($CoAs_2$), containing from 3 to 24 per cent. of cobalt, and from 0 to 35 per cent. of nickel; also as cobalt-glance, bright white cobalt ($CoAsS$), containing from 30 to 34 per cent. of cobalt. Cobalt is prepared on a large scale as a metal at Iserlohn, and at Pfannenstiel, near Aue, in Germany. Metallic cobalt exhibits a steel-grey colour, somewhat verging upon red, a strong metallic lustre, assumes a brilliant polish, is malleable and ductile, and far tougher than iron. It requires a very high temperature for fusion, is only slowly acted upon by dilute acids, but readily dissolved by nitric acid and aqua regia.

Cobalt Colours. The ores intended for the manufacture of the cobalt colours are roasted for the double purpose of volatilising the sulphur and arsenic they contain, and for effecting the oxidation of the cobalt. After roasting, the ores are known as Zaffer or Saphera. According to the degree of purity, the trade distinguishes the ores as "common," "medium," and "very fine;" they contain essentially a mixture of proto-peroxide of cobalt, arsenic, nickel, and traces of the oxides of manganese and bismuth, and are used in the preparation of cobalt-colours. In Sweden "zaffers" are prepared by precipitating a solution of sulphate of protoxide of cobalt with a solution of carbonate of potassa. Zaffer is used for the manufacture of smalt, cobalt, ultramarine,—a misnomer, for evidently ultramarine is contracted from *ultra-mare*, because the lapis lazuli was brought across the seas from India—Cæruleum, Rinnman's-green (cobalt-green or Saxony-green), and also cobalt-yellow, cobalt-violet, and cobalt-bronze.

Smalt. Compounds of cobalt have the property of imparting a blue colour to glassy substances at a red heat; when, therefore, impure protoxide of cobalt is fused with silica and carbonate of potassa, the result is the formation of an intensely blue-coloured glass, which when pulverised is known as *smalt*. This substance was discovered and first prepared by the Bohemian glass-blower, C. Schürer, who lived in the sixteenth century. Smalt is now prepared by melting the roasted cobalt ores with quartzose sand and potash, in crucibles placed in a glass-furnace. The red-hot glass produced is quenched in cold water to render it brittle. It is next pulverised and scoured with water, by which operation smalts are obtained of different degrees of fineness, not simply as regards minute state of division, but also depth of colour, all of which varieties abroad—where to a limited extent the smalt is still used though it is almost entirely superseded by artificially-made ultramarine—bear distinctive names. It has been proved experimentally that the colouring-matter of smalt is potassio-silicate of protoxide of cobalt, in which the proportion of the oxygen of the acid to that of the base is as 6 : 1. According to M. Ludwig, 100 parts of the undermentioned cobalt colours contain:—

	Norwegian Smalt.	German Smalt.	
	High colour.	Termed high Eschel.	Coarse and pale coloured.
Silica	70·86	66·20	72·11
Protoxide of cobalt ..	6·49	6·75	1·95
Potassa and soda	21·41	16·31	1·80
Alumina	0·43	8·64	20·04

These substances, moreover, contain small quantities of protoxide of iron, lime, protoxide of nickel, arsenic acid, carbonic acid, water, and oxides of lead and iron. Dr. Oudemans lately analysed a beautifully ultramarine-coloured sample of smalt, which was found to contain 5·7 per cent. of protoxide of cobalt. As cobalt-glass obtained with soda is never of a pure colour, that alkali cannot replace potassa in the manufacture of smalt. Since the roasting of the cobalt ores is not continued long enough to oxidise the nickel contained in them, that and some other metals present fuse during the preparation of the smalt, and, settling to the bottom of the crucible, form an alloy termed Cobalt-speiss.

Cobalt Speiss. This substance is of a reddish-white hue, has a strong metallic lustre, is fine-grained in structure, and contains on an average from 40 to 56 per cent. nickel, 26 to 44 per cent. arsenic, as well as copper, iron, bismuth, sulphur, &c. Dr. Wagner found that (1870) a sample of this alloy from a Saxon mine contained in 100 parts:—

Nickel	48·20
Cobalt	1·63
Bismuth	2·44
Iron	0·65
Copper	1·93
Arsenic	42·08
Sulphur	3·07
	100·00

The material is chiefly used for the preparation of nickel.

Applications of Smalt. Smalt is still employed in washing and dressing blue, and for imparting a blue tint to paper. It is not, however, very suitable for this purpose, as, on account of its hardness, it soon destroys the points of writing pens. Smalt is more extensively used for blue-enamelling glass, porcelain, and earthenware.

Cobalt Ultramarine. This substance, also known as Thénard's blue, is a pigment consisting of alumina and protoxide of cobalt. Curiously enough this pigment has been discovered and prepared at three several periods and localities by different people; first, by Wenzel, at Freiberg, Saxony; next by Gahn, at Fahlun, Sweden; and lastly, simultaneously at Paris and Vienna, by Thénard and Von Leithener. The pigment is prepared either by mixing solutions of alum and a salt of protoxide of cobalt, precipitating the mixture by a solution of carbonate of soda; or by the decomposition of aluminate of soda by means of chloride of cobalt. The ensuing precipitate, consisting of an intimate mixture of hydrate of alumina and hydrate of protoxide of cobalt, is first well washed, then dried and heated for some time. The pigment thus produced is, when seen in daylight, of course after pulverisation, very similar to ultramarine, but by artificial light its colour is a dirty violet. It is, however, not acted upon by acids, as distinguished from artificial ultramarine; neither is it affected by alkalies nor heat, as is copper or mineral blue. Cobalt-ultramarine, chiefly under the denomination of Thénard's blue, is employed as a paint in oil- and water-colours, and also for staining glass and porcelain.

Cæruleum. Is a pigment prepared in England, exhibiting a bright blue colour, not changing in artificial light, and consisting of stannate of protoxide of cobalt (SnO_2,CoO), mixed with stannic acid and gypsum in the proportions, in 100 parts, of 49·6 of oxide of tin, 18·6 protoxide of cobalt, 31·8 gypsum. This pigment is not affected by heat, or the action of dilute acids and alkalies; nitric acid dissolves the proxtoxide of cobalt, leaving the other ingredients, from which the gypsum may be cleared by water.

Rinmann's or Cobalt-Green. This substance, also known as cobalt-green, zinc-green, and Saxony-green, is a compound similar to the cobalt-ultramarine, for the alumina of which oxide of zinc is substituted. This green is prepared by mixing a solution of white vitriol with a solution of a salt of protoxide of cobalt, precipitating by carbonate of soda, and washing, drying, and heating the precipitate. This pigment when pure contains 88 per cent. of oxide of zinc and 12 per cent. of protoxide of cobalt. It is not affected by strong heat, tinges the borax-bead blue, dissolves in warm hydrochloric acid, forming a blue colour, which, upon water being added, becomes a pale red. Treated with caustic potassa, the oxide of zinc is dissolved, and may be detected, after previous dilution with water, by the addition of a solution of sulphuret of potassium.

Chemically Pure Protoxide of Cobalt. This substance is occasionally employed for the preparation of fine colours. It may be obtained by heating one part of previously roasted and finely-pulverised cobalt ore with two parts of sulphate of potassa until no more sulphuric acid is given off. The fused mass, consisting of sulphate of potassa, sulphate of protoxide of cobalt, and insoluble arsenical salts, is, when cooled, first treated with water, and next digested with hydrated protoxide of cobalt to precipitate any iron which may happen to be present, and in order to eliminate the oxide of that metal the solution is filtered. It is next precipitated with carbonate of soda, and finally the precipitate is washed and heated.

Nitrate of Protoxide of Cobalt and Potassa. This double salt, known by its trade name of cobalt-yellow, is obtained by mixing a solution of protoxide of cobalt with nitrite of potassa; it is a yellow crystalline precipitate, perfectly insoluble in water. M. Saint-Evre first investigated this body, and struck with its beautifully yellow colour, quite like that of *purrhee* (euxanthinate of magnesia), and with the fact that cobalt-yellow resists oxidising and sulphuretting influences, suggested its applicability to artistic purposes. He prepares this pigment by precipitating with a slight excess of potassa the double salt of protoxide of cobalt and potassa, obtaining a rose-red-coloured protoxide of cobalt and potassa. Into this thickish magma deutoxide of nitrogen gas is passed. According to Hayes, this pigment is readily obtained by causing the vapours of hyponitric acid to pass into a solution of protonitrate of cobalt, to which some potassa has been added; the whole of the cobalt is then converted into cobalt-yellow. As the nitrite of protoxide of cobalt and potassa can be obtained even from impure solutions of protoxide of cobalt, so as to be quite free from any nickel, iron, &c., the use of this preparation of cobalt is preferable for glass and porcelain staining, when a pure blue is required.

Cobalt-Bronze. This substance, a double salt of phosphate of protoxide of cobalt and ammonia, prepared at Pfannenstiel, near Aue, in Saxony, has been but lately brought into commerce. It is a violet-coloured powder, very much like the violet-coloured chloride of chromium, and exhibits a strong metallic lustre.

NICKEL.

($Ni = 59$; Sp. gr. $= 8{\cdot}97$ to $9{\cdot}25$).

Nickel and its Ores. This metal occurs in the following ores:—Copper nickel or arsenical nickel, $NiAs$, containing about 44 per cent. Ni.; antimonial nickel, $NiSb$, with about 31·4 per cent. Ni.; white arsenical nickel, $NiAs_2$, with about 28·2 per cent. Ni; in some varieties of cobalt speiss, as, for instance, the capillary pyrites (sulphuret of nickel) with 64·8 per cent. Ni); and the antimonial nickel-ore,

$$NiS_2+Ni(Sb,As_2),$$

with about 26·8 per cent. Ni. There is found at Rewdansk, Oural, Russia, a mineral known as Rewdanskite, a silicate of hydrated protoxide of nickel (12·6 per cent. Ni), from which the metal is obtained. Nickel is also extracted from ores which contain it accidentally, as, for instance, some species of iron and copper pyrites, cobalt-speiss, and certain copper ores known as Mansfield ores, which yield sulphate of nickel as a by-product. Several varieties of manganese contain nickel and also cobalt; and in England the residues arising from the manufacture of chlorine are in some instances applied in the production of these metals, the process yielding, according to Gerland, 2·5 kilos. of nickel and 5 kilos. of cobalt for 1 ton of manganese. Some magnetic iron ores yield nickel, a specimen of such ore from Pragaten, Tyrol, Austria, containing, according to M. T. Petersen, 1·76 per cent. of NiO.

Preparation of Nickel from its Ores.

It very rarely happens that the natural ores of nickel are so pure, that is to say, contain the metal in such a state of combination, as to admit of the direct extraction of the metal, and therefore, as is the case with copper, a preliminary operation is required, which aims at the concentration of the metal in combination either with sulphur, in which case the combined substance is termed regulus, and sulphuret of iron is applied as a means of concentrating the nickel contained in the ore as sulphuret: or, if the nickel happens to be combined chiefly with arsenic, the concentrated mass is termed speiss; while in a few instances an alloy of nickel and coarse or black copper is obtained. From all these products the metallic nickel, or sometimes an alloy of nickel and copper, is prepared by the dry or moist process.

The method of obtaining nickel embraces two distinct features, viz.:—

I. A smelting process, which aims at rendering the nickel of the ores richer, and concentrating the metal—

- α. In a regulus.
- β. In a speiss, or
- γ. In alloy with coarse or black copper.

II. In the separation of the nickel, or a definite alloy from the products obtained by the concentration-smelting; this can be done—

- a. By the dry, or
- b. By the hydro-metallurgical method.

As it is found that the preparation of an alloy of copper and nickel for the manufacture of so-called German-silver, impairs the most valuable properties of nickel—its white colour and resistance to chemical action—the obtaining of pure metallic nickel is preferred.

The Concentration-Smelting of the Nickel Ores.

I. This operation is carried on (a) for regulus, when the nickel-ores are mixed with iron pyrites and magnetic pyrites, and consists in smelting the previously partly roasted ore with quartz or substances rich in silica. During the process the greater portion of the oxide of iron generated is absorbed by the slag, while the nickel, also first oxidised, and more readily reduced than the oxide of iron, is converted to the metallic state and taken up by and concentrated in, the regulus, a mixture of undecomposed sulphurets of metals and reduced sulphates. If at the time the ore contains copper, that metal is even more readily and completely incorporated with the regulus than the nickel itself. If the roasted mass contains too much protoxide of iron, a portion of that metal is reduced, and either taken up by the regulus, or separated as containing nickel. The separation of the iron from the regulus frequently requires the application of a refining furnace provided with a blast so as to oxidise the iron. A better result is obtained by treating the previously roasted ore in a reverberatory furnace with quartz, heavy spar, and charcoal or coal; sulphuret of barium results, which, becoming converted into baryta, transfers its sulphur to the oxides of nickel and copper, while the baryta forms with the quartz and protoxide of iron a readily fusible slag. At Dillenburg an ore which contains the sulphurets of nickel to about 7·5 per cent., and copper, is treated in the following manner:—It is roasted in stacks, built not unlike coke-ovens; next broken up and smelted in a low-blast furnace heated by means of coke, no other ingredients being added, as the ore contains silica, alumina, and lime in sufficient quantities, so as to obtain crude regulus (I.) This crude regulus is next melted with slags, so as to obtain concentrated regulus (II.) It is lastly submitted to the action of a refining blast-furnace in order to lessen the quantity of iron, care being taken to leave enough sulphur to keep the refined regulus (III.) brittle; finally, the regulus is employed in the manufacture of nickel and alloys of nickel. Composition—

	I.	II.	III.
Nickel	19	24	35
Copper	13	39	43
Iron	35	12	2
Sulphur	33	25	20
	100	100	100

This mode of operation is employed at Klefver (Sweden), and in some other localities.

(β). The smelting of nickel ores for the purpose of concentrating the metal in speiss is applied when the nickel occurs in combination with either arsenic only or with that metal and antimony, such compounds being occasionally obtained in the operations of smelting copper, lead, and silver ores, and as by-products of the smelting of metals not containing arsenic, as, for instance, in slags from copper-smelting, in which case there is added arseniuret of iron (arsenical iron pyrites, $FeAs + FeS_2$, which when heated by itself splits up into As and $2FeS$). When a mixture consisting of nickel, iron, and arsenic is first submitted to a partial calcination, and next to a simultaneously reducing and fusing smelting, the iron is taken up by the slag, the nickel-oxide is reduced, and the arseniates are converted into arseniurets, and as the nickel has a greater affinity for arsenic than for sulphur, the speiss will also take up that metal. If the compound originally operated upon happens to contain copper, that metal is present in the speiss, from which it may be separated as a sulphuret by the addition of ordinary pyrites to the arsenical pyrites during the smelting. By frequently roasting and smelting the speiss, aided occasionally by an oxidising blast and the use of heavy spar and quartz as slag, the iron is gradually eliminated. At Birmingham, Hungarian and Spanish nickel ores are smelted for speiss, these minerals containing on an average from 40 to 55 per cent. of nickel, and from 30 to 40 per cent. of arsenic, as well as sulphur, bismuth, and copper.

(γ). Smelting for the concentration of coarse copper or nickeliferous pig-iron. When the quantity of nickel contained in the copper ores is very small, the nickel accumulates in the first portions of the refined copper in such quantities as to repay the trouble of extraction. M. Wille analysed some refined copper, obtained from the cupriferous slate of Riechelsdorf, and found it to contain from 7·8 to 13·6 per cent. of nickel; occasionally the surface-discs of rosette-copper contain crystals of protoxide of nickel.

Preparation of Metallic Nickel, or of Alloys of Nickel and Copper.

II. This is effected by submitting the product of the concentration-smelting to either (*a*) a dry method of treatment, or (*b*) a hydro-metallurgical process.

(*a*). Preparation of nickel by the dry method. It appears that the methods hitherto employed have not led to very satisfactory results; it is true that when nickel-speiss is, as suggested by M. von Gersdorf, repeatedly roasted with charcoal-powder and wood-shavings, oxide of nickel is obtained, and may be reduced by means of coal, coke, or charcoal; but as this oxide is always mixed with arseniate of oxide of nickel, the metal also contains arsenic, and any German-silver made with it is brittle and turns brown on exposure to air; moreover, a small quantity of iron is always present in the nickel thus prepared. A better result is obtained by the process proposed by the late H. Rose, in 1863, for the preparation of the metal free from arsenic, and which consists in mixing the pulverised speiss with sulphur, and heating this mixture, thereby forming sulphuret of nickel and sulphuret of arsenic, the latter being volatilised. This operation is repeated as often as may be necessary; the sulphuret of nickel is roasted, and sulphate of protoxide of the metal is formed, which, at a high temperature, as is the case with protosulphate of iron, loses its sulphuric acid, leaving the oxide of nickel to be reduced to the metallic state by means of charcoal. At Dillenburg experiments have been made in order to obtain from what is termed a refined stone—a compound of nickel, copper, iron, and sulphur—an alloy of nickel and copper, by first completely calcining the sulphurets, and so driving off the free sulphur; next mixing the remainder of the substance in quantities of 100 lbs. with 45 lbs. of soda, and submitting this mixture to the heat of a reverberatory furnace in order to render the sulphur soluble in water as sulphuret of sodium and sulphate of soda, leaving an alloy which, of course, has to be refined in order to eliminate the last traces of iron.

(*b*). Obtaining nickel by the wet, or hydro-metallurgical method. A preliminary roasting of the ores or products of metallurgical operations containing nickel is required in order to convert the iron into an oxide soluble in acid, and to convert the nickel, copper, and cobalt, either into sulphates soluble in water or into oxides or basic salts, both of which are soluble in sulphuric and hydrochloric acids. From any such solution the nickel is precipitated by a suitable reagent, either as oxide or as sulphuret, and from these materials metallic nickel or an alloy of that metal with copper is prepared. The preparation of nickel by the moist method consists of three different operations:—1. The preparation of the nickel solution. When nickeliferous and metallurgical products are roasted, either with or without the addition of copperas, the result is the formation of the sulphates of iron, copper, nickel, and cobalt, and this mixture when roasted becomes decomposed, the sulphuric acid being driven off first and most readily from the sulphates of the oxides of iron, and with greater difficulty from the sulphate of protoxide of cobalt. Accordingly, after roasting, the mass on being treated with water, yields the larger portion of the nickel and cobalt with some of the copper, while the greater part of the latter, with very small quantities of cobalt and nickel, and the whole of the iron, remain undissolved as oxides; by the use of acids the protoxides of copper and nickel are extracted from this residue. If the roasted material is immediately treated with hydrochloric acid, the result is that more of the oxide of copper than of the protoxide of nickel is dissolved; but by again treating the residue with boiling acid the oxides of iron and nickel are extracted. Speiss may be used for obtaining a nickel solution by first heating the previously roasted speiss with a mixture of soda and nitrate of soda, next extracting the arseniate of soda by means of water, and afterwards treating the residue with sulphuric acid, roasting the sulphates obtained so as to decompose only that of iron, and finally treating the mass again with water to obtain the sulphates of nickel and cobalt in solution. According to Professor Wöhler's plan, the arsenic of the speiss can be removed by fusion with sulphuret of sodium, and a subsequent treatment with water, in which it, as a sulpho-salt, is soluble. 2. The nickel may be precipitated from the solution in various ways. According to M. Stapff's plan (1858), a fractioned precipitation may be obtained by means of chalk employed at various temperatures, the result being that first iron and arsenic, and next copper, are separated, so that only the nickel remains in solution, and can be thrown down by milk of lime. According to M. Louyet (1849), iron and arsenic are first precipitated by milk of lime mixed with bleaching-powder, and the liquid containing this precipitate filtered off. From the acid filtrate the bismuth, lead, and copper that may be present are removed by sulphuretted hydrogen; the filtrate from these joint sulphides is next boiled with bleaching-powder, the cobalt being separated as a peroxide, and the nickel remaining in solution. If it is desired to obtain the cobaltic peroxide in a pure state, the precipitation should be so conducted as to leave a little cobalt with the nickel, no injury therefrom accruing to that metal. At Joachimsthal, Bohemia, the nickel is precipitated from the acid solution after the removal of the copper by sulphuretted hydrogen, by means of bisulphate of potassa as bisulphates of protoxide of nickel and potassa, leaving the cobalt in solution free from nickel, which in its turn is thrown down by carbonate of soda. 3. The conversion of the nickeliferous precipitate into metal, or into an alloy with copper, may be carried out in the following manner:—The protoxide of nickel is first separated from the liquid by filtration, then pressed so as to admit of its being dried by intense heat, and next ground up with water and washed with very dilute hydrochloric acid, in order to remove the gypsum, of which some 8 to 12 per cent. is mixed with the oxide. The oxide is then made with beet-root sugar, molasses, and coarse rye-meal, into a stiff paste, which is shaped into cubes from 1·5 to 3 centimetres in size; these cubes are next rapidly dried, and after drying are placed with charcoal powder in crucibles, or in perpendicular fire-clay cylinders, where, being submitted to a very strong white heat, the metal is reduced, an operation which, in the case of the alloy of copper and nickel, or of cupriferous nickel, is finished in 1½ hour, the reduction of the pure metal taking fully three hours. The copper soon becomes molten, but the nickel only sinters together, on account of the very great infusibility of this metal. The small cubical pieces of nickel as met with in commerce exhibit externally a strong metallic lustre, produced by putting the cubes with water into casks, which are made to rotate. In order to ensure uniformity of composition, and hence a good sale for the alloy of copper and nickel, rosette-nickel, care is taken to procure the mixture of the two metals in the proportion of 66·67 per cent. copper, and 33·33 per cent. nickel, while the cubical nickel contains from 94 to 99 per cent. of pure metal. At a nickel-oven at Dillenburg, the metal is not made into cubes, but treated in the same way as rosette-copper.

Properties of Nickel. Pure nickel has a nearly silver-white colour, with a slight yellowish hue, is very difficult to melt, rather hard, very ductile, and easily polished; sp. gr. = 8·97 to 9·26. When quite pure this metal may be drawn into wire, rolled into sheets, hammered, and forged; its tensile strength stands to that of iron as 9 : 7. Nickel is analogous to iron, but distinguished from it by possessing a greater power of resisting chemical agents; on this account, and for its not becoming rusty in air or when in contact with water, nickel is used for obtaining silver-like alloys (see Copper). In Belgium, Switzerland, the United States, and Jamaica, small coins have been made of an alloy of nickel with zinc and copper, pure nickel being too hard to admit of readily coining. An alloy known as *tiers-argent*, one-third silver, consists in 100 parts of:—

Silver	27·56
Copper	59·06
Zinc	9·57
Nickel	3·42
	99·61

The total annual production of nickel on the Continent of Europe amounts (1870) to 11,200 cwts., exclusive of what is made in England. Very pure nickel is obtained at Val Bénoit, near Luik, Belgium, from an Italian nickel ore, the metal containing less than 1 per cent. impurities.

COPPER.

($Cu = 63{\cdot}4$; Sp. gr. = $8{\cdot}9$).

Copper, where it occurs, and how. Copper is one of the metals met with most abundantly. It has been known from a very remote antiquity—even before iron—and bears the Latin name *Cuprum*, because it was obtained by the Romans and Greeks from the Island of Cyprus; from the Latin name of this metal the English, German, Dutch, and French names are derived. Copper is found to some extent in a metallic state naturally, but it is chiefly obtained from ores, among which the oxides and sulphides are the chief.

Ores of Copper. Native copper is found in large quantities near Lake Superior, in North America; and in Chili there is known a peculiar kind of sand called copper-sand, or copper-barilla, consisting of from 60 to 80 per cent. of metallic copper, and 20 to 40 per cent. of quartz. This sand is imported into England and smelted, with other copper ores, at Swansea.

Red copper or (suboxide, or red oxide of copper), Cu_2O, containing 88·8 per cent. of copper, is met with in octahedrical-shaped crystals, disseminated or instratified through rock in Cornwall. An intimate mixture of suboxide of copper and iron-ochre is known as tile-ore, or earthy-red oxide of copper. Azurite, or blue copper ore, containing 55 per cent. of copper, is a compound of carbonate of protoxide of copper and hydrated protoxide ($2CuCO_3 + CuH_2O_2$). It occurs in beautifully blue-coloured crystals disseminated through rock and gangue in Cornwall, and was formerly found at Chessy, near Lyons.

Malachite, containing 57 per cent. of copper, consists of basic carbonate of hydrated oxide of copper ($CuCO_3 + CuH_2O_2$), and occurs in rhombic crystals, also as stalactite and stalagmite, and in Atlas ore, a veined and earthy ore called copper-green or earthy malachite, and very frequently with azurite in Australia and Canada.

Copper-glance, copper-glass, sesquisulphuret of copper (Cu_2S), contains 80 per cent. of the metal. Purple copper ore, variegated copper ore, a compound of copper-glance and sesquisulphuret of iron ($3Cu_2S + Fe_2S_3$), with 55·54 per cent. of copper and copper pyrites ($Cu_2S + Fe_2S_3$ or $CuFeS_2$), with 34·6 per cent. of copper are the chief sulphur ores used in the extraction of copper. Copper pyrites is often mixed with iron pyrites, and also often contains silver and nickel. The mineral known as Bournonite, although a lead ore, often contains as much as 12·76 per cent. of copper.

Slaty copper ore is a bituminous marly schist belonging to the Permian formation, through which sulphuretted copper ores are disseminated; this ore is chiefly found in Germany.

Grey or black copper ores, so called Fahl ores, are compounds consisting of electro-positive sulphurets, viz., sulphuret of copper and of silver, with electro-negative sulphurets, viz., those of arsenic or antimony. As these ores contain silver they are usually considered as silver ores, the quantity of copper contained in them amounting to about 14 to 14·5 per cent. Atacamite is also a copper ore ($3CuH_2O_2 + CuCl_2$), containing 56 per cent. of copper. This substance is chiefly met with in Chili and other parts of the Western Coast of South America, in Southern Australia, and in Peru, and in that country it is ground to powder and used instead of sand or sawdust to strew on the floors of rooms. It is imported in that state under the name of Arsenillo, and is smelted with the atacamite in lumps at Swansea.

Mode of treating the Copper Ores for the Purpose of Extracting the Metal. It is quite evident that the treatment of the ores must vary according to the constitution of the metals. The ores in which copper is contained as oxide, or ochrey ores, are reduced readily enough by simple treatment with carbonaceous matter and a flux; but these ores are by no means abundantly found, and are, therefore, usually mixed with pyritical sulphuretted ores. The smelting of copper from its ores therefore embraces:—

1. The smelting from ores containing oxides.
2. From pyritical ores, and
3. The hydro-metallurgical method.

Pyritical copper ores are smelted either in a shaft, or pit-furnace, or in a reverberatory furnace. In the latter instance the reduction of the metallic regulus of copper obtained from a previous roasting of the ore, is effected by the aid of sulphur, not by that of coal. The regulus is gradually rendered richer and richer in metal, until at last the decomposition of the sulphur is completed by the action of the oxygen of the air; by this operation suboxide is plentifully formed, and as a consequence the metallic copper obtained is in the state technically termed "over-refined." When the shaft-furnace is employed, the first portion of the operation is similar to that alluded to, but the metal is reduced with coal or charcoal, and hence the copper obtained—leaving out of the question the presence of the foreign metals—is never over-refined, but contains carbonaceous matter, so that in order to render the copper, as it is technically termed, tough—that is to say, malleable when cold as well as when hot, another operation is required, which it is evident from the foregoing must differ for the two qualities of crude metal.

The Working-up of the Copper Ores in the Shaft Furnace. The ores are first roasted or calcined, and a portion of the sulphur, arsenic, and the antimony they contain volatilised; sulphates of the metals as well as arseniates and antimoniates are at the same time formed, while a portion of the ore is not acted upon at all. When the smelting operation is commenced, fluxes are added, and any oxide of copper present is reduced to the metallic state, while simultaneously the sulphates are again converted into sulphurets, which jointly with the metallic copper form the rather richer crude regulus of copper; while if arsenic and antimony prevail speiss is formed. The more readily oxidised metals present, chiefly iron, form, as protoxides, compounds with the fluxes. By a repetition of this process with the coarse metal regulus—the operation being known as a concentration-smelting—there are obtained thin matt, and what is termed black copper, containing foreign metals, which are got rid of by a first or coarse refining, a portion of the impurities under the influence of a high temperature, the oxygen of the air and fluxes, being partly volatilised, partly taken up in the slag. The copper obtained by this operation, rose- or disc-copper, contains, because the calcination is carried rather too far, suboxide of copper, which impairs the ductility of the metal. This defect is remedied by a rapid smelting under a layer of charcoal, the suboxide being reduced and tough copper obtained. When a reverberatory furnace is employed, the coarse and last refinings are usually included in one process.

According to the Continental methods, the calcined ore is smelted and converted into coarse regulus in a shaft-furnace, the fuel employed being charcoal or coke, or a mixture of the two. Fig. 18 exhibits the vertical section of the furnace; Fig. 19 is a front view, the front wall being removed to show the interior construction. Fig. 20 exhibits the lower part of this furnace; *t t* are the tuyere-holes for the blast; the apertures, *o o*, placed just above the lowest part of the breast of the hearth, communicate by means of channels with the smelting-pots, c′ c′, the object being to gradually collect the molten contents of the furnace. Since copper ores always contain more or less iron, it might happen that by simply employing a reducing smelting, some of that metal would become mixed with the copper; in order to avoid this, fluxing materials rich in silica are added, with which the protoxide of iron forms a readily fusible slag. The oxides of copper present in the calcined materials are reduced to the metallic state by the sulphuret of iron—

FIG. 18.

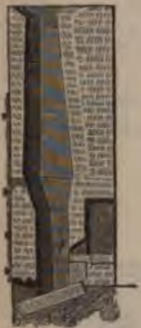


FIG. 19.

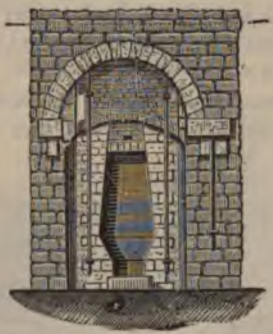
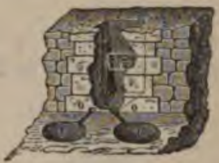


FIG. 20.



$$3CuO + FeS = SO_2 + FeO + 3Cu.$$

The metal regulus, a mixture of sulphurets of copper and iron and other metals, containing on an average 32 per cent. of copper, collects in the lower part of the furnace, and the slag formed is called crude or coarse slag. The roasting of the regulus aims at its most complete oxidation, while the sulphur is eliminated. The calcined regulus is next smelted in a shaft furnace with the addition of a flux, a process technically known as concentration-smelting.* The refined regulus obtained by this smelting contains some 50 per cent. of copper, and is next treated to obtain black-copper, coarse metal. But if the regulus contain a sufficient quantity of silver, that metal is extracted by methods which will be fully elucidated when silver is treated of; in some cases this operation is combined with the extraction of lead from the copper, and effected by what is termed liquidation, of which more presently.

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* There are no equivalent terms in English to express the real meaning of the German words, a fact which is readily accounted for, if we consider that these operations are essentially German and of very ancient standing.

The operation of smelting for a refined regulus is omitted if tolerably pure copper ores are operated upon, and such ores after calcination are immediately treated in a low blast-furnace to obtain the black-copper. In addition to black-copper, a thin matt containing from 93 to 95 per cent. of that metal is obtained. As an instance of the composition of black-copper, we quote Dr. Fach's analysis of a sample of that material produced at Mansfeld, in 1866; in 100 parts there are:—

Copper	93·49
Lead	1·49
Zinc	1·47
Iron	1·03
Nickel and cobalt together	1·25
Silver	0·03
Sulphur	0·99
	99·75

Refining the Copper. The black-copper is next submitted to an energetic oxidising smelting process in order to get rid of the impurities in the slag. This process is carried on either—

1. In a small refining furnace;
2. In a large refining furnace; or
3. In a reverberatory furnace.

Refining on the Hearth. 1. This operation is effected in a furnace or hearth, represented in vertical section in Fig. 21, and in perspective in Fig. 22; *a* is a semi-globular excavation, termed the crucible; *b* is a cast-iron bed-plate; *h* represents one of the two tuyeres by means of which a blast is conveyed to the fuel and the surface of the copper. The black or coarse copper is melted by the heat of charcoal aided by the blast, the sulphur, arsenic, and antimony being volatilised, while the oxides of iron and of the other non-volatile metals are taken up with the suboxide of copper by the slag, which gathers at the surface of the molten metal, and is from time to time removed. As soon as the refining is complete, the blast is turned off and the surface of the copper, the metal being heated far above its melting-point, covered with charcoal-dust. When cooled sufficiently, water is poured on, and a portion of the metal thus suddenly solidified admits of being lifted off from the rest of the molten mass in cakes or discs, technically known as rose or rosette-copper; this operation is repeated until the crucible contains no more metal.

Fig. 21

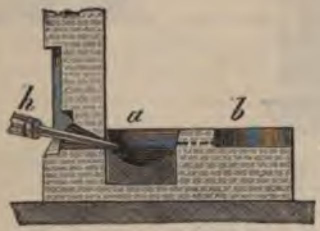
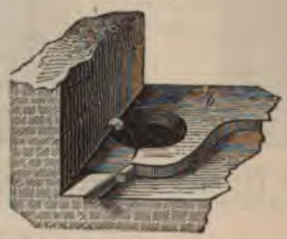


Fig. 22

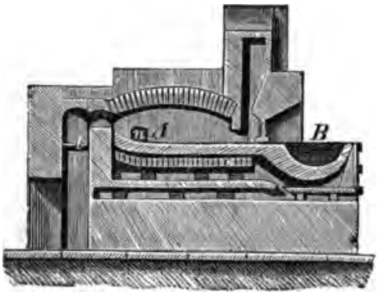


Refining Copper in large quantities. As the refining of copper on the hearth has been found to yield but poor results, another contrivance, shown in vertical section in Fig. 23, is now more generally employed. A is the smelting-hearth; B the refining crucible, of which there are two; *n*, the opening for the tuyere of the blast; *l*, the furnace. The mode of operation is similar to that just given. When the refining is complete the molten metal is run into the crucibles, and after having cooled sufficiently, water is sprinkled on and the discs of rose-copper lifted off. For the reason that in this kind of reverberatory furnace the copper is not, as is the case on the hearth, in contact with the fuel, the result is a purer metal.

Liquation Process. When the copper ores contain silver, the black copper is submitted, before being refined, to a process known as liquation, unless it should be preferred to extract the silver by the Ziervogel method (see Silver). The liquation process is based upon the fact that lead and copper may be melted together, but do not remain alloyed on cooling, so that a compound is formed containing much more copper than lead, the remainder of the lead separating and, while taking up the silver, settling down in consequence of its specific gravity. When the molten mass is slowly cooled, the lead combined with the silver runs off after the solidification of the copper; but if the molten metals are rapidly cooled, an intimate mixture of the two takes place. The mode of separating the silver from the lead will be referred to when treating of the former of these metals.

It has been already mentioned that the refined copper resulting from the above processes contains suboxide of that metal, which, if amounting to a quantity of 1·1 per cent., renders the copper unfit for use at ordinary temperatures, by impairing its ductility and malleability while if the quantity of the suboxide amounts to 1¼ per cent., the metal is unfit for use both cold and at a red heat—that is, becomes cold- and red-short. This condition of the metal is, in Germany, termed "over-cooked," and the remedy is simply to melt the copper and submit it to what is, in England, technically known as poling; that is to say, a sufficiently long, stout, and green piece of wood, is used for thoroughly stirring up the molten mass. The *rationale* is that the carbon and hydrogen contained in the wood deoxidise the suboxide at the high temperature, rendering the metal very malleable and ductile, making it, as is technically termed, *tough*. A sample of Mansfeld refined and toughened copper was found by Dr. Steinbeck to contain in 100 parts:—

FIG. 23.



Copper	94·37
Silver	0·02
Nickel	0·36
Iron	0·05
Lead	0·60
Oxygen	0·58
Sulphur	0·02
	100·00

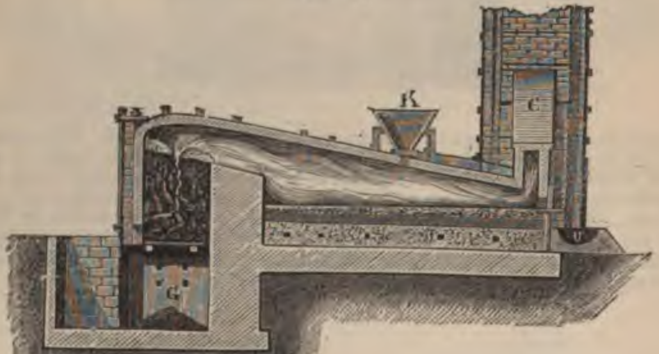
English Mode of Copper Smelting. Owing chiefly to the possession of an enormous wealth of coal, the fuel most suited for the reverberatory furnaces, a method of copper-smelting peculiar to England is pursued, and a metal obtained of a very superior quality, although not so good as that extracted from particular ores in Russia and Australia. Swansea is the chief and most important seat of this industry in the United Kingdom, and to it copper ores are not only carried from Cornwall, North Wales, Westmoreland, Anglesea, and other portions of the realm, Ireland included, but are imported from Chili, Peru, Cuba, Norway, Australia, and other parts of the world. The English ores are mainly pyritical.

The chief processes of this mode of smelting consist in—1. Calcination of the ore; 2. Smelting for coarse metal; 3. Calcination of coarse metal; 4. Making of white metal, a concentration process in which calcined coarse metal is smelted with rich ores; 5. Preparation of the blue metal by smelting together calcined coarse metal and calcined ores of medium richness; 6. Preparation of a red and white metal by smelting together the slags of the previous operations; 7. Calcination of the blue metal (5) and preparation of white extra metal; 8. Calcination of the white extra metal and preparation of the concentration metal; 9. Calcination of the ordinary white metal of cupriferous residues for the purpose of obtaining blistered copper. According to M. Gurlt's views, all these operations may be reduced to, at most, two calcinations and three smelting operations, viz.:—1. Calcination of the previously pulverised ores with the addition of common salt, or of chloride of calcium, to form volatile chlorides; 2. The smelting of calcined ores and obtaining a more liquid slag and a coarse metal; 3. The calcination of coarse metal by the aid of a blast for the production of blistered copper with or without the addition of chlorides; 4. Refining and toughening the blistered copper.

Calcining, or Roasting the Ores. This operation as carried on at Swansea does not materially differ from that pursued on the Continent. No very appreciable loss of weight is experienced, as the weight of the oxygen taken up compensates for the loss occasioned by the more or less complete volatilisation of the sulphur, antimony, arsenic, &c. The roasted ore is black, this colour being due to the oxides of iron and copper. During the roasting heavy white fumes are emitted, consisting of sulphurous and arsenious acids mixed with other substances; more recently, calcining furnaces have been constructed on Gerstenhöfer's patent system, so as to admit of the utilisation of the sulphurous acid for the manufacture of sulphuric acid.

Smelting the Ores. This operation is effected at Swansea in a furnace of which Fig. 24 exhibits a sectional view. K is a funnel intended for the introduction of the roasted ore; G is an ash-pit filled with cold water. The object in view is to separate the ores from the gangue as well as from oxides other than that of copper, by causing the sulphur of the sulphurets remaining undecomposed to act upon a portion of the oxides and sulphates in such a manner that these are either taken up by the slag, as, for instance, the oxide of iron, or are again reduced to sulphide, as the oxide and sulphate of copper. At a higher temperature the oxide of copper is reduced to the metallic state by the action of the sulphurets of iron and copper, oxide of iron forming, and the metallic copper being partly

FIG. 24.



taken up by the regulus, partly converted into suboxide again by the peroxide of iron, which is converted into protoxide and dissolved by the siliceous matter. The product of the first stage of the smelting is a coarse metal, regulus.

Roasting or Calcining the Coarse Metal. The roasting of the coarse metal is performed in the reverberatory furnace used for the first calcination of the ores. The objects in view are the oxidation of any metallic iron present, and the partial volatilisation and combustion of the sulphur, partial only, for otherwise the smelting for white metal would be impeded or not performed without serious loss of copper.

Smelting for White Metal. This operation consists in mixing the previously calcined coarse metal with rich copper ores containing hardly any sulphuret of iron, but consisting chiefly of the sulphide and oxide of copper mixed with quartz in such proportion that the pyrites (copper) is oxidised by the oxygen of the oxides present, the result being that all the copper combines with the coarse metal, while the protoxide of iron forms with the quartz silicate of protoxide. The white metal, almost entirely consisting of (Cu_2S), is run into cakes in sand-moulds.

Blistered, or Crude Copper. The white metal obtained is converted into blistered copper by placing it on the hearth of a reverberatory furnace, and causing the fire to act at first rather gently, but afterwards so as to fuse the mass, the total duration of the process for each charge being 12 to 14 hours; the result is the volatilisation of the sulphur in the form of sulphurous acid, and the elimination, partially by volatilisation, partially by their being taken up in the slag, of such impurities as arsenic, cobalt, nickel, tin, iron, &c. When the mass becomes fused, suboxide of copper and sulphide of copper mutually decompose, the result being the formation of sulphurous acid and metallic copper ($2Cu_2O + Cu_2S = SO_2 + 6Cu$).

The molten coarse metal, impure copper as yet, is run into moulds, and its surface becoming covered with black-coloured vesicles, due to the escape of gases and vapours from the molten metal, it is termed blistered copper. On being broken, after cooling, it exhibits a honeycombed structure, due to the same cause that produces the blistered appearance on the surface. Blistered copper, as usually obtained, is comparatively pure.

Refining the Blistered Metal. The last operation in the English method of copper-smelting is the refining of the blistered metal in a reverberatory furnace, care being again taken to fire at first gently, so that the metal shall not become molten until after some six hours. As soon as the entire charge is thoroughly melted down, the slag, rich in suboxide of copper, is tapped off, and the molten metal covered with charcoal-powder. The operation of poling (see above) is then performed, birch-wood being preferred for the purpose; this done, the copper having been run into moulds of a rectangular shape, is known as refined tough cake.

Mode of obtaining Copper from Oxidised Ores. Copper is readily obtained from oxidised ores by smelting them in a shaft-furnace with coke or coal, and such fluxes as will produce a slag which does not absorb copper. The crude metal obtained is refined in a low-blast-furnace. The smelting of oxidised ores is limited to a few localities, among which the Oural and Siberian works are the most important. Large quantities of excellent and very rich oxidised copper ore are found, but not as yet wrought, in the islands of Timor and Timor-Laout, and the adjacent islands of Polynesia.

Hydrometallurgical Method of Preparing Copper. This method owes its existence to the application of practical and analytical chemistry to metallurgy. As copper is very readily obtained, even from ores too poor to admit of being treated by the dry process, in such a state of combination as to admit of its being dissolved in water, and thrown down from this solution by the simple presence of metallic iron, the hydrometallurgical process is often advantageously applied, One of the oldest of hydrometallurgical methods is that known as the cementation-process, performed by precipitating copper from a solution of the sulphate of the metal by means of metallic iron. Solutions of the sulphate occur naturally in some mines, and are also artificially prepared by treating poor oxidised copper ores with sulphurous acid, or by exhausting these ores with hydrochloric or dilute sulphuric acids, or by roasting pyritical ores and exhausting them with water. The copper obtained by this process is called cementation-copper. In the island of Anglesea the cementation liquid is conducted first into large basins in order that the ochrey and other suspended matters may subside, and afterwards

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is run into the cementation tanks containing old scrap-iron intended to serve as a precipitating agent. This scrap-iron is occasionally stirred up, so as to renew the metallic surface presented to the solution. The muddy liquid, containing spongy metallic copper and impurities, is run into reservoirs intended for the deposition of the spongy mass, which, after the supernatant liquid is run off, is dried in a furnace. The material contains on an average only 15, but may contain from 50 to 65 per cent. of copper. The main body is usually composed of basic sulphate of iron, which is effectually removed by the application of stirring machinery, such as is used in breweries in the mash-tubs. At Rio Tinto, Spain, and at Schmöllnitz, Hungary, cementation-copper is prepared on a very large scale. In Norway, copper solutions are treated, according to Sinding's plan, with sulphuretted hydrogen, and the precipitate either worked up for metallic copper, or for sulphate of copper.

Instead of sulphur, large quantities of iron pyrites containing more or less copper are burnt, and the sulphurous acid obtained applied in the manufacture of sulphuric acid. The spent pyrites is frequently treated hydrometallurgically with a solution of chloride of iron, the copper being precipitated by means of sulphuret of iron. Poor ochrey copper ores are often worked up to obtain sulphate of copper, by some method suitable to the locality; for instance, roasting with iron pyrites or with copperas. It pays in some instances to roast pyritical copper ores, and after roasting to treat them for obtaining cementation-copper.

Copper obtained by Voltaic Electricity.

Copper electrolytically precipitated is, provided pure materials are operated upon, and the galvanic current not too strong, the purest obtainable. This method has been proposed and even tried on a large scale in Italy, in order to save time and iron, and to throw down the copper of the cementation-tanks. It is a generally known and daily applied fact that copper, as a coherent mass, can be separated from sulphate of copper electrolytically.

Properties of Copper.

The peculiar and really beautiful red colour of copper, the only metal so distinguished, is too well known to need mention. It is, although a hard and tough metal, so ductile and malleable that it may be drawn out to the very finest wire, and beaten to extremely thin leaves. Its malleability is increased by increase of temperature, and at a low red heat it can be hammered, rolled, and beaten into any required shape. Its fracture is granular. Its sp. gr. is = 8·9; one cubic metre weighs about 8900 kilos. Its melting-point, according to Pouillet, 1200°; to Daniell, 1400°. The latest and most careful researches on this topic have been made by Dr. von Riemsdijk at the Utrecht Mint, and he has found that chemically pure copper fuses in an atmosphere of hydrogen at 1330°; that is to say, at a temperature higher than the melting-point of either gold or silver, as simultaneously determined by an extensive series of experiments made in atmospheres of hydrogen. If properly poled, as the term runs, or in other words, free from suboxide, copper, when molten, flows readily, but when mixed with suboxide the flow is sluggish. While in the molten state the surface of the metal exhibits a beautiful sea-green colour. Copper is not suited for the making of castings, and probably this is due to a peculiar effect of heat upon this metal, as many of its alloys, especially those with tin, are very suited for casting. Molten copper suffers great expansion on cooling, and becomes honeycombed and internally crystalline. This defect can only be remedied by either keeping the metal while molten under a layer of charcoal, or by cooling it to some extent before casting into moulds, which should be made of a good conducting material, so as to cause the rapid cooling of the metal. Iron moulds, internally coated with a layer of bone-ash, are the best. Small quantities, 0·1 per cent. of zinc, lead, potassium, and other metals added to the molten copper entirely deprive it of the property of expanding and becoming honeycombed on cooling; the same effect is observed when copper holds in solution a small quantity of suboxide, but this fact is not available for any practical use, as such copper is cold-short. Just before cooling the vessel exhibits the phenomenon of spirting, the flying about of small globules of copper, accompanied, if large quantities of the metal are treated, by a distinctly audible report. This phenomenon appears to be due to a cause similar to that producing it when silver is operated upon, viz., the violent expulsion of previously absorbed oxygen. At a very high temperature, and with free access of air, or under the influence of electricity, copper burns, giving a brilliant green flame. In countries where, as in Sweden, Russia, and Holland, the roofs of churches and other large buildings are covered with copper—the most expensive at the first outlay, but the most lasting material for roofing purposes—the phenomenon of the burning of copper is now and then witnessed on a very large scale when fires accidentally occur. Copper-filings are used in pyrotechny, for producing a green flame. Dry air does not affect copper, unless sulphuretted hydrogen and other sulphurous emanations are present; but moist air causes the copper to become covered with carbonate of hydrated suboxide of copper, verdigris, or rust. Experience has proved, in the case of copper roofs, that this material protects the subjacent metal, and adheres to it with great tenacity. When solid masses of copper are heated they at first assume an iridescent rainbow hue, and next become covered with a brownish-red coloured suboxide, which, if the heating is continued, becomes black oxide, technically known as copper-ash, or copper-forge scale. In order to remove this oxide, when the copper is to be rolled into sheets, &c., the metal is dipped into what is termed a pickle—a solution of ammonia and common salt, and on being taken out is brushed with a heather-broom. Copper, as usually met with in commerce, is not by any means pure, but contains variable quantities of other metals, among which are chiefly iron, antimony, arsenic, lead, tin, zinc, and sulphur; Dr. Reischauer found in perfectly malleable copper no less than 1·48 per cent. of impurities insoluble in nitric acid. If this quantity is only slightly increased, the quality of the copper is so impaired that it is not only unfit for being rolled and hammered, but also for casting statues (always alloyed), because such copper loses its peculiar colour, and does not withstand atmospheric influences. Copper is largely used for various purposes, among which we name only a few—vacuum and other pans in sugar-works; distillery, brewery, and other apparatus; for covering wooden sea-going vessels, and for a variety of generally well-known purposes. Dr. Steinbeck found that refined Mansfeld copper, analysed 1868, contained in 100 parts—

Copper	99·28
Silver	0·02
Nickel	0·32
Iron	0·06
Lead	0·12
	100·00

The total annual production of copper over the entire globe amounts (1870) to 1,300,000 cwts., of which England alone yields fully 350,000 cwts.

Alloys of Copper. There are several alloys of copper, among which bronze, brass, and German, or nickel silver, are the chief.

Bronze. Alloys, consisting of copper and tin, or of copper, tin, and zinc, or of copper and aluminium, all bear the name of bronze. The addition of any of these metals to copper renders it more fluid when molten, and hence better suited for castings, as well as denser, and consequently more easily polished; alloys are harder, more sonorous, and (the aluminium alloy excepted), far cheaper than copper itself. The addition of from 0·12 to 0·50 per cent. of phosphorus to these alloys renders them more homogeneous and malleable. The chief varieties of bronze in use are known as (α) bell-metal, (β) gun-metal), and (γ) statuary metal.

(α). Bell-metal consists on an average of 78 parts of copper and 22 parts of tin. It should be sonorous, hard, and strongly cohesive. Being a brittle alloy it cannot be worked on the lathe; hence the desired sound or musical note of a bell depends entirely upon the shape given in the casting, and upon the constituents of the alloy. In order to save tin, zinc and lead are sometimes added, but too much of these impairs the goodness of the alloy. It is an error to mix silver with this alloy, in order to render it highly sonorous; analyses made of bell-metal cast in the middle ages in various countries, prove the absence of silver from such metal, traces only being present as an impurity.

(β). Gun-metal consists on an average of 90 parts of copper and 9 of tin. This alloy should combine mechanical and chemical durability. As regards its mechanical properties, the metal should be:—1. Tough, so as to prevent the piece or gun bursting while the charge is being fired, during which operation the metal is exposed to a pressure of from 1200 to 1500 atmospheres. 2. Elastic, so that the gun may be able to yield to some extent to the smart shocks occasioned by the evolution of gas during firing. 3. Hard, so that the motion of the ball should not cause any damage to the interior of the gun. As regards chemical durability, the alloy must resist the action of air and of the products of combustion of powder and gun-cotton at high temperatures. Gun-metal answering these requirements is unfortunately subject to what is termed liquation; that is to say, while in the molten state it separates into two qualities of alloy, one more fluid and containing more tin than the other. This separation makes the casting of guns in this alloy a difficult matter, because the homogeneity of the mixture is uncertain. It appears, however, that the addition of from 0·12 to 0·5 per cent of phosphorus remedies the defect. Gun-metal, however, is fast being superseded by steel in the manufacture of ordnance. MM. Maritz, at the Hague, have for several generations been renowned for the superiority of their gun-metal manufacture, which is still pursued by them. According to a statement in the "Handwörterbuch der Chemie" (Art. "Geschütz-metall,") the alloy employed by them consists of 0·69 per cent. Fe, 88·61 per cent. Cu, and 10·70 per cent. Sn; generally the quantity of tin amounts to from 9 to 11 per cent.

(γ.) Statuary-bronze for ornamental purposes consists of copper, tin, lead, and zinc. It is requisite that while molten this alloy should be very fluid, so as to fill every part of the mould. After cooling, the metal must admit of being chiselled, and by exposure to air it should assume what is termed patina—a peculiar greenish black hue. The statue of Louis XIV. at Paris, made 1699, consists of—copper, 91·40; zinc, 5·53; tin, 1·70; lead, 1·37. The statue of Henri IV. on the Pont Neuf at Paris, consists of—copper, 89·62; zinc, 40·20; tin, 5·70; lead, 0·48. Aluminium-bronze (90 parts copper and 10 aluminium) is used for various ornamental purposes, chiefly in imitation of gold.

Brass. This alloy has been known from a very remote period. Zinc and copper form various alloys, but brass only is technically applied, and contains on an average 30 per cent. of zinc. The colour of the alloy is inclined to red, when the quantity of zinc is small, and to yellow or whitish-yellow when the quantity of zinc is increased. The ductility and malleability of the alloy increase with the quantity of copper. Brass may be hammered, rolled into sheets, or drawn to wire while cold, but cannot be worked hot. The so-called yellow metal, Muntz's patent, an alloy of 40 parts of zinc and 60 of copper, may be wrought while red-hot, rolled into sheets, and forged into bolts. It is chiefly used for marine purposes, including the internal lining of air pumps of marine steam-engines. Brass is not so readily oxidised as copper, being harder, tougher, more easily fusible, and more fluid while molten. It solidifies without becoming honeycombed, and hence is suited for making all kinds of castings; while simply by the addition of from 1 to 2 per cent. of lead, it is capable of being readily worked on the lathe, and may be then filed without, as it otherwise does, clogging the teeth of the file.

Brass is made by any of the following methods:—1. By melting together a mixture of calamine stone and black or blistered copper under a layer of charcoal. 2. By simply melting together zinc and refined copper. The first method is the oldest, and is still carried on in furnaces arranged so that they may contain from 7 to 9 fire-clay crucibles at the same time. These crucibles are filled with the necessary materials, viz., previously roasted zinc ore, or residues from zinc-smelting furnaces, and copper. As by the use of calamine stone, only some 27 to 28 per cent. of zinc can be imparted to the alloy, it is usual to add, previously to pouring out the molten alloy, another quantity of calamine stone, rather to prevent any loss of zinc by ignition than to increase the quantity of that metal. In former times the manufacture of brass was carried on in two distinct operations, one being the preparation of an alloy containing only 20 per cent. of zinc, known as arco-smelting, and the other the conversion of the arco into brass by a second smelting, and the addition of zinc. At the present time the manufacture of brass consists in simply placing alternate layers of copper and zinc in fire-clay or graphite crucibles, and then smelting the two metals under a thick layer of charcoal. The alloy is cast in granite moulds surrounded by a thick coating of clay and cow-dung, or sand-moulds. Occasionally sheet-copper is converted into brass by exposing the sheets to the fumes of metallic zinc. Among brass alloys we may notice the following:—Tomback, or red brass, consisting of 85 parts of copper and 15 of zinc. Dutch-gold, a gross misnomer, as none of it is made in Holland, and as the term really applies to a very pure gold coin, the ducat, still made, although not current, in Holland, at the Utrecht Mint. The brass alloy thus named consists of 11 parts of copper and 2 of zinc, and is made chiefly at Nürnberg and Fürth, Bavaria, for the purpose of being beaten into very thin leaves. The alloy termed Aich-metal, and consisting of 60 parts of copper, 38·2 parts of zinc, and 1·8 parts of iron, is in reality malleable brass. Sterro-metal, though very much harder, is similar to the foregoing in composition.

The well-known yellow, or Muntz, metal, largely used in this country for marine purposes, coating ships, &c., is an alloy of copper and zinc in proportions varying from 50 per cent. of zinc and 63 of copper, to 39 per cent. of zinc and 50 per cent. of copper. The alloy in use for coins of small value in this country, France, and Sweden, consists of 95 parts of copper, 4 parts of tin and 1 of zinc. The alloy used for this purpose in Denmark consists of 90 parts of copper, 5 of tin, and 5 of zinc. Bath-metal, or white brass, consists of 55 parts of copper and 45 of zinc. An alloy used for buttons consists of 20 parts of copper and 80 parts of zinc. The bronze colours (powdered alloys of copper and zinc), now largely used for bronzing painted surfaces, as well as for lithochromy and various other purposes, are obtained from scraps of metal rubbed down with oil, tallow, or wax, and turpentine. The various beautiful colours, violet, copper-red, orange, gold-yellow, green, are due to partial oxidation. These bronze-colours are not to be confounded with a beautiful substance known as mosaic gold—*aurum musivum*—bisulphide of tin. Analyses show the proportions in these alloys to be—

For bright colours	Copper ..	83
	Zinc.. ..	17
For red or deeper colours ..	Copper ..	94—90
	Zinc.. ..	6—10
For copper-red colours		100

Chemical analysis has also proved the quantity of copper to amount to—

a. In French bronzes:	Copper-red colour	97·32 per cent.
	Orange	94·44 „
	Bright yellow	81·29 „
β. In English bronzes:	Orange	90·82 „
	Deep yellow	82·37 „
	Bright yellow	80·42 „
γ. In Bavarian bronzes:	Copper-red	98·92 „
	Violet	98·82 „
	Orange	95·30 „
	Deep yellow	81·55 „
	Bright yellow	82·34 „

German or Nickel silver.

German, or nickel silver, also called Argentan, packfong, or white copper, is an alloy of copper with nickel and zinc, or tin, and may be considered as a brass to which from one-sixth to one-third of nickel has been added. This alloy appears to have been known in China from a very remote period; in Europe it has been more generally in use during the last thirty years. The colour is nearly silver-white; its fracture small-grained and compact; sp. gr. = 8·4 to 8·7. It is harder, but yet quite as ductile as ordinary brass, and takes an excellent polish. It is prepared by melting together the granulated metals, zinc, copper, and nickel; these metals are put into a crucible in such a manner that copper is at the bottom as well as the top, while a layer of charcoal-powder covers the whole. Care is taken to stir the mass with an iron rod. Nickel-silver of good quality has the appearance of a silver alloy, containing one-fourth of copper. Nickel-silver is capable of assuming an excellent polish, and is not readily acted upon by vinegar and the ordinary acids in culinary use; hence it is used for spoons and forks.

Average German-silver consists of—

Copper	50—66·0
Zinc	19—31·0
Nickel	13—18·5

At Sheffield the following varieties of this alloy are made:—

	Copper.	Nicke	Zinc.
Common	8	2	3·5
White	8	2	3·5
Electrum	8	4	3·5
Infusible	8	6	3·5
Tutenac	8	3	6·5

When tried on the touchstone, nickel-silver is hardly distinguishable from the silver alloy just mentioned, but on applying nitric acid to the streak caused by the nickel alloy, it is more rapidly dissolved, and by adding a few drops of chloride of sodium solution no turbidity, or precipitate of chloride of silver, is produced on the stone. The alloy known as Alfénide, used for making tea-pots, sugar-basins, milk-ewers, and similar articles, is nickel-silver, thickly electro-plated with pure silver, the quantity of silver amounting to about 2 per cent. The alloy, known as *tiers-argent* (one-third silver), consists, according to Dr. C. Winkler's analysis (see "Chemical News," vol. xxii., p. 225), of—Copper, 59·06; silver, 27·56; zinc, 9·57; nickel, 3·42.

Since 1850 the Swiss Confederation has brought into circulation a series of small coins (*monnaie billon*) which contain in 1000 parts:—

	Silver.	Copper.	Zinc.	Nickel
Pieces of 20 Rappen	150	500	250	100
" 10 "	100	550	250	100
" 5 "	50	600	250	100

These coins are not turned red by wear, but assume a yellowish hue. In Belgium the 5, 10, and 20 centime pieces are made of an alloy of 25 parts of nickel and 75 parts of copper; while the United States' cent pieces contain 12 parts of nickel and 88 of copper. The alloy known on the Continent as Suhler's white copper, consists of 88 parts of copper, 8·75 parts of nickel, and 1·75 parts of antimony.

Amalgam of Copper. By the name of metallic cement is understood an amalgam of 30 parts of copper and 70 parts of mercury. It is obtained by moistening pulverised copper, obtained in a spongy state, by reducing its oxide at a low red heat, by means of hydrogen with nitrate of suboxide of mercury, care being taken to incorporate this saline solution thoroughly with the copper, while adding hot water. This cement, at first soft, hardens in a few hours. It has been successfully applied in stopping decayed teeth.

PREPARATIONS OF COPPER.

Blue Vitriol. Sulphate of Copper. This salt is met with naturally in kidney-shaped masses, or as an outer covering of minerals containing copper, as well as in solution, as referred to under Cementation-copper. Sulphate of copper, blue- or Cyprus-vitriol, crystallises in the shape of triclinohedrical blue-coloured crystals, soluble in 2 parts of hot and 4 of cold water, and insoluble in alcohol. 100 parts of the salt contain:—

Sulphuric acid	32·14
Oxide of copper	31·79
Water	36·07

Formula:—$CuSO_4 + 5H_2O$.

Preparation of Blue Vitriol. Chemically-pure sulphate of copper is obtained by heating metallic copper with concentrated sulphuric acid; the metal is oxidised by a portion of the oxygen of the acid, while sulphurous acid escapes ($Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$). If the metal is previously converted into oxide of copper by exposure to a red heat, only half the quantity of sulphuric acid is required. Sulphate of copper is manufactured on a large scale by any of the following processes :—1. By the evaporation of cementation-water until crystallisation is attained. 2. By heating sheets of copper in a reverberatory furnace to the boiling-point of sulphur; a quantity of that element being then thrown in, and the flues and other openings closed, the effect is the formation of sulphide of copper (Cu_2S), which is converted by a comparatively low heat and the action of the oxygen of the air into sulphate ($Cu_2S + 5O = CuSO_4 + CuO$). The mass is next placed in a suitable vessel, and as much sulphuric acid is added to it as is sufficient to saturate the oxide of copper. The clear solution, having been decanted from the insoluble residue, is set aside for crystallisation. 3. By treating the crude copper obtained by smelting the ores, and containing about 60 per cent. of metal, with sulphuric acid. The resulting solution is evaporated in leaden vessels, and the clear liquid left to crystallise in copper pans. From the mother-liquor of the crystals metallic copper is precipitated by means of iron, because the presence of a large quantity of sulphate of iron renders this mother-liquor unfit for the further making of blue-vitriol. This method of obtaining sulphate of copper is the least expensive, but the salt is not quite pure, containing, according to M. Herter's analysis of Mansfeld blue-vitriol, about 3 per cent. of sulphate of iron, and 0·083 per cent. of metallic nickel. Very frequently the scraps and refuse of copper smithies, copper-scale, and other residues of that metal, are used in preparing sulphate of copper. 4. At Marseilles, malachite is dissolved in sulphuric acid to obtain blue-vitriol. 5. In Norway, iron pyrites containing copper are roasted and treated with water, the copper contained being precipitated with sulphuretted hydrogen, and the sulphide of copper, when dry, converted into sulphate by exposure to a gentle heat. 6. Large quantities of sulphate of copper are obtained as a by-product of silver-refining, especially when silver is treated for the purpose of extracting the gold it contains, by boiling—usually silver coins, chiefly Mexican and Peruvian dollars—with strong sulphuric acid; sulphate of silver and, as the coins contain some copper, the sulphate of that metal, are formed, while the gold is left as an insoluble substance. The silver is reduced to the metallic state ($Ag_2SO_4 + Cu = CuSO_4 + 2Ag$) by means of sheets of copper placed in the acid solution, which is previously diluted, and which, after having been decanted from the sediment, spongy metallic silver, yields on evaporation a very pure sulphate of copper. 7. Sulphate of copper is also obtained as a by-product of the hydrometallurgical process of extracting silver, or Ziervogel's process. In order to separate the sulphate of iron from the crude blue-vitriol, as obtained at copper-smelting works from various cupriferous refuse, the crude salt is roasted so as to bring about a partial decomposition. By this means the sulphate of iron is decomposed, and the oxide of that metal formed is insoluble in water. The saline mass is dissolved in water, and the clear solution, decanted from the sediment, evaporated to crystallisation. According to Bacco's plan, the crude blue-vitriol is dissolved in water, and carbonate of copper added to the solution, to cause the precipitation as oxide of all the iron present, while an equivalent quantity of oxide of copper is dissolved and converted into sulphate. The purified sulphate of copper solution having been filtered is evaporated and left to crystallise.

Double-Vitriol. Under the name of double-vitriol, a mixture of the sulphates of copper and iron crystallised together, and sometimes containing white vitriol, is met with on the Continent. The Salzburg vitriol, known by the brand of a double eagle, contains about 76 per cent., the Admont 83 per cent., and the double Admont 80 per cent. of sulphate of protoxide of iron. Of later years, however, these vitriols have been less in demand.

Applications of Blue-Vitriol. As the base of the pigments obtainable from copper, the sulphate is very frequently used, and should be pure, or at least free from the sulphates of iron and zinc. Blue-vitriol also serves for the manufacture of acetate of copper, for bronzing iron, for bringing out the colour of alloys of gold. It is used in dyeing and printing in various ways, for galvano-plastic purposes, and during the last twenty years large quantities of this salt have been sent to Mexico and Peru to be applied in the American amalgamation-process of extracting silver.

Copper Pigments. Among the many pigments which owe their blue or green colour essentially to copper, we may treat of the following:—1. Brunswick-green. 2. Bremen-green and Bremen-blue. 3. Casselmann's-green. 4. Mineral-green. 5. Schweinfurt-green, also known as emerald-green. Many of the pigments mentioned here by their German names are known in this country by other denominations, but are not for that reason any different in composition.

Brunswick-Green. Under this name several compounds of copper are applied as oil-paints. The pigment now chiefly in use bearing this name is basic carbonate of oxide of copper ($CuCO_3 + CuH_2O_2$), an imitation of mountain- or mineral-green, and obtained from either finely pulverised malachite or the sediment often met with in cupriferous cementation-liquids. Brunswick-green is prepared on a large scale by the decomposition of sulphate of iron by means of either carbonate of soda or carbonate of lime, and in other cases by the decomposition of chloride of copper by means of a carbonated alkali. The ensuing precipitate is washed with boiling water, and afterwards mixed with a smaller or larger quantity of sulphate of baryta, zinc-white, or gypsum, and frequently with Schweinfurt-green (aceto-arsenite of copper) in order to obtain the desired hue. Another variety of Brunswick-green, rarely met with in the present day, appears to be a kind of artificially-prepared atacamite, an oxychloride of copper, the formula of which is, according to Ritthausen, $CuCl_2,3CuO + 3H_2O$.

Bremen-Blue, or Bremen-Green. These substances are essentially hydrated oxide of copper, and are met with as a very bright blue spongy mass with a greenish hue. The value is greater according to the finer blue colour and loose spongy texture. When used with water, gum, or glue, this pigment yields a bright blue colour, hence its first name; but when it is mixed with linseed-oil, the blue colour turns within twenty-four hours to green, in consequence of the saponification of the oxide of copper, which becomes oleate, palmitate, and linoxate of that base. Bremen-green occurs in various hues obtained by mixing the precipitate with well-cleansed gypsum. At the present time the pigment is generally obtained from oxychloride of copper ($CuCl_2,3CuO + 4H_2O$). This preparation may be made in various ways, provided care be taken that the light green paste—technically known as oxide—contains no protochloride of copper (Cu_2Cl_2). Gentele's method is as follows:—

1. 112·5 kilos. of common salt, and 111 kilos. of sulphate of copper, both free from iron, are ground together with sufficient water to promote reaction. 2. 112·5 kilos. of old copper sheeting is cut into pieces a square inch in size, and placed with water acidulated with sulphuric acid in rotating casks so as to remove all rust, oxide and oxychloride, from this metal, which is next washed with water. 3. The clean metal thus obtained is next placed in what is known as oxidation-closets, and covered for a thickness of half-an-inch with the paste mentioned above. A mutual action, aided by that of the atmosphere, is set up, the result being that the chloride of copper first takes up copper, becoming protochloride; this in its turn takes up oxygen from the atmosphere and water, and thus becomes converted into the green-coloured insoluble basic hydrated oxide of copper, the action being greatly aided by the turning over of the mass with a copper spade every two or three days. As the treatment of protochloride of copper with alkalies or alkaline earths gives rise to the separation of red or yellow-coloured suboxide, the mass should not, on being tested and previous to further operations, yield even the faintest indication of the presence of suboxide, since the slightest trace would spoil the hue of the pigment to be obtained; consequently in some works the pasty mass is left for years before it is used for further operations. The action is accelerated by causing the mass to become dry before turning it over with the spade; the consequence being that the air gets thorough access, and a complete oxidation is obtained in about three to five months time. The mass is then cleansed with the smallest possible quantity of water, and is thus separated from the non-oxidised

metallic copper. 4. To some 6 gallons of this cleansed material are added 6 kilos. of hydrochloric acid, and this mixture is allowed to stand for about two days. 5. Into a tank or tub—the blue tub—are poured some 15 gallons clear colourless potassa-lye. This having been done, the acid mixture is first diluted with some 6 more gallons of water, and then, as rapidly and expeditiously as possible, poured into the blue tub, the mixture being continuously stirred. The result of this last operation is that the previously basic copper compound, converted by HCl into neutral cupric chloride, is, when brought in contact with the potassa, converted into blue-coloured oxyhydrate of copper or Bremen-blue, while chloride of potassium is also formed. 6. After the mass has become pasty, it is left to stand for a couple of days, and then thoroughly washed by decantation to remove the chloride of potassium. The cupric oxyhydrate is then put on cloth filters, kept moist, and exposed to the air for some time. It is next dried at a temperature of from 30° to 35°, since at a higher temperature the hydrate of the oxide by losing its water becomes blackish-brown coloured. It is clear that Bremen-blue can be differently obtained, but these differences of preparation do not bear so much upon the precipitation of the hydrated oxide as upon the means of obtaining chloride of copper; these means may of of course be varied in many ways; for instance, by causing a mixture of common salt, dilute sulphuric, and copper scraps to act upon each other, the mass being afterwards exposed to the action of the air; by the action of hydrochloric acid upon copper and its oxide; or by partly decomposing neutral nitrate of copper by means of carbonate of soda. In this case a precipitate of carbonate of copper is formed, which, while giving off its carbonic acid, becomes converted into basic nitrate of copper ($CuN_2O_6 + CuH_2O_2$), deposited as a heavy green powder. A solution of zinc-oxide of potassa (solution of zinc-white in caustic potassa), is next added, the result being the formation of a deep blue pigment, very spongy and very *covering* (a technical term in use by painters); consisting of zincate of copper, with a small quantity of basic nitrate of copper. A magnesia Bremen-blue is obtained by the precipitation of a solution of the sulphates of magnesia and copper, to which some cream of tartar is added, by means of potassa, care being taken to pour the saline solution into the alkaline, and to keep an excess of the latter.

Casselmann's-Green. In the year 1865 Dr. Casselmann discovered this pigment, a beautiful green free from arsenic. It is prepared by mixing together boiling solutions of sulphate of copper and an alkaline acetate; the resulting precipitate is a basic salt of copper ($CuSO_4 + 3CuH_2O_2 + 4H_2O$). After drying, this salt is, next to Schweinfurt-green, the finest of all colours obtained from copper, and being free from arsenic, is highly commendable, though yet poisonous, as are most preparations of, and especially acetates of, copper.

Mineral-Green and Blue. This pigment, also known as Scheele's-green, is not so frequently used now as formerly. It is essentially a mixture of hydrated oxide of copper and arsenite of copper, and does not cover very well. It is prepared by dissolving 1 kilo. of pure sulphate of copper in 12 litres of water, to which is added, whilst constantly stirred, a solution of 350 grms. arsenious acid and 1 kilo. of purified potash (carbonate) in 8 litres of water. The resulting grass-green coloured precipitate is washed with boiling water and dried. Another pigment, sometimes known as mineral-green, is obtained from pulverised malachite, or basic hydrated oxide of copper. By the term mineral-blue is generally understood a kind of Berlin-blue, rendered less deep coloured by the addition of pipe-clay or other white-coloured powders, but the term also applies to a pigment formerly obtained by grinding and washing the purest pieces of lazurite of copper, a mineral

$$(2CuCO_3 + CuH_2O_2)$$

found in the Tyrol and near Lyons. This pigment is artificially obtained in France, Holland, and Belgium, by precipitating a solution of nitrate of copper with caustic lime or caustic potassa, and afterwards mixing the previously washed precipitate with chalk, gypsum, or heavy spar. The pigment is sent into the trade for use chiefly as a water-colour. Under the name of lime-blue a similar preparation occurs in quadrangular lumps, obtained by precipitating a solution of 100 parts of sulphate of copper and 12½ parts of sal-ammoniac with a milk of lime containing 30 parts of caustic-lime. The precipitate is a mixture of hydrated oxide of copper and sulphate of lime, according to the formula ($2CaSO_4,2H_2O + 3CuH_2O_2$). This pigment exhibits a purer tint than Bremen-blue, but though it covers pretty well as a water-colour, it is almost useless as an oil-colour.

Oil-Blue. A pigment which, when ground with oils and varnishes, yields a beautiful violet-blue, and is essentially composed of sulphide of copper (CuS), there being applied in its manufacture either the native mineral, known as cupreous indigo, or an artificially prepared sulphide, obtained by fusing finely divided metallic copper with hepar-sulphuris, a mixture of several sulphurets of potassium. The fused mass is treated with water, and the sulphide of copper remains in small blue-coloured crystals, which, after drying, are pulverised and mixed with oil.

Schweinfurt-Green, or Emerald-Green. This pigment is by far the most beautiful, but also the most poisonous, of all green-coloured copper pigments. In Germany this substance is known under a number of aliases derived from the peculiar depth of hue as modified in various manufactories by means of sulphate of baryta, sulphate of lead, and chrome-yellow. The constitution and mode of preparation of this pigment remained, at least on the Continent, a trade secret until the researches of MM. Braconnot and J. von Liebig made the particulars known. According to Dr. Ehrmann, pure emerald- or Schweinfurt-green is an aceto-arsenite of copper :—

$$\left.\begin{matrix}(C_2H_3O)_2\\ Cu\end{matrix}\right\}O_2+3(CuO,As_2O_3);$$

in 100 parts—Oxide of copper, 31·29; arsenious acid, 58·65; acetic acid, 10·06, Dr. R. Wagner states that this formula is only empirical, because a portion of the copper is present as suboxide, and a portion of the arsenic as arsenic acid.

According to Dr. Ehrmann's statement, this pigment is prepared by first separately dissolving equal parts by weight of arsenious acid and neutral acetate of copper in boiling-water, and next mixing these solutions while boiling. There is immediately formed a flocculent olive-green coloured precipitate of arsenite of copper, while the supernatant liquid contains free acetic acid. After a while the precipitate becomes gradually crystalline, at the same time forming a beautifully green pigment, which is separated from the liquid by filtration, and after washing and carefully drying is ready for use. The mode of preparing this pigment on a large scale was originally devised by M. Braconnot, as follows:—15 kilos. of sulphate of copper are dissolved in the smallest possible quantity of boiling-water and mixed with a boiling and concentrated solution of arsenite of soda or potassa, so prepared as to contain 20 kilos. of arsenious acid. There is immediately formed a dirty greenish-coloured precipitate, which is converted into Schweinfurt-green by the addition of some 15 litres concentrated wood-vinegar. This having been done, the precipitate is immediately filtered off and washed. It thus appears that the preparation of this pigment aims first at the least expensive preparation of neutral arsenite of copper, which is next converted into aceto-arsenite by digesting the precipitate with acetic acid. The pigment is available as a water- and an oil-colour, but does not cover very well in oil, although it dries rapidly. The colour cannot be used for mural painting, as the lime absorbs the acetic acid, leaving a yellowish-green arsenite of copper. The Schweinfurt-green consists of microscopically small crystals; if these crystals are pulverised, the colour, previously grass-green, becomes paler. Air and light do not affect this pigment, which is insoluble in water, but becoming, when boiled with it for a length of time, brown-coloured, probably in consequence of the loss of some acetic acid. It is a well-known fact that paper-hangings containing this pigment, and pasted on damp walls, cause the inmates of the rooms to suffer from headaches, due in all likelihood to volatile arsenical emanations, among which is arseniuretted hydrogen.

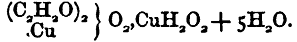
Stannate of Oxide of Copper. This preparation, also known as Gentele's-green, is obtained by precipitating a solution of sulphate of copper with stannate of soda, washing and drying the precipitate, which forms a beautifully green, innocuous, at least as compared with the foregoing, copper pigment.

Verdigris. Under this name we meet in commerce with a neutral and a basic acetate of copper; the one, a crystalline substance is

$$\left.\begin{matrix}(C_2H_3O)_2\\ Cu\end{matrix}\right\}O_2+H_2O,$$

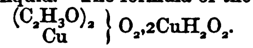
a salt formerly only prepared in Holland, and designated as "distilled verdigris," in order to mislead as to its mode of manufacture.

The basic salt, blue verdigris, is chiefly prepared at and near Montpellier, by employing the marc of the grapes, the skin and stems of the bunches after the juice has been squeezed out, which readily forms acetic acid by fermentation. Into the marc are placed sheets of copper previously moistened with a solution of acetate of copper. The metal becomes coated with a layer of verdigris, which is removed by scraping. It is next kneaded with water, after which the paste is put into leathern bags and pressed, so as to obtain rectangular cakes. The metal is treated in the same manner until it is entirely converted into basic verdigris, having a blue colour, and known as French-verdigris. Formula—



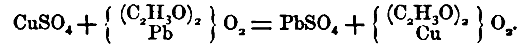
$$\left.\begin{matrix}(C_2H_2O)_2\\ Cu\end{matrix}\right\} O_2,CuH_2O_2+5H_2O.$$

A green-coloured verdigris is obtained at Grenoble and elsewhere, by submitting sheets of copper to the action of vapours of vinegar, or by placing the metal between pieces of coarse flannel soaked with that liquid. The formula of the substance thus produced is—



$$\left.\begin{matrix}(C_2H_3O)_2\\ Cu\end{matrix}\right\} O_2,2CuH_2O_2.$$

Neutral acetate of copper, first made by the Saracens in Southern Spain, and since the middle of the fifteenth century by the Hollanders, is now obtained either by—1. Dissolving the basic salt in acetic acid. 2. Or by the double decomposition of sulphate of copper and acetate of lead:—



$$CuSO_4+\left\{\begin{matrix}(C_2H_3O)_2\\ Pb\end{matrix}\right\} O_2=PbSO_4+\left\{\begin{matrix}(C_2H_3O)_2\\ Cu\end{matrix}\right\} O_2.$$

By the first method the basic acetate is dissolved in 4 parts of acetum distillatum (purified vinegar) or in wood-vinegar, the liquid being placed in a copper cauldron and heat applied. The clear liquid is decanted, and then evaporated in copper pans until a saline crust makes its appearance, when the fluid is transferred to wooden vessels provided with thin laths serving as a solid nucleus for the crystals. According to the second plan, the solutions of the two salts are mixed, the liquid decanted from the sediment of sulphate of lead, and next evaporated after the addition of some acetic acid, until a crust of the salt is formed. Instead of acetate of lead, the acetates of lime and baryta are now used. The neutral acetate of copper is met with in commerce in "bunches" (grappes), consisting of deep green-coloured, non-transparent crystals, soluble in 13·4 parts of cold, in 5 parts of hot water, and in 14 parts of boiling alcohol. This salt, like the basic acetates, is highly poisonous.

Applications of Verdigris. Both basic and neutral are employed as oil-and water-colours. In Russia verdigris, mixed with white-lead, is frequently used as an oil paint, the result being the formation of carbonate of copper and basic acetate of lead. The former of these substances yields with the undecomposed white-lead a bright blue colour, which, after painting, turns to a peculiarly fine green, the usual colour of the iron roofs of the houses in Russia, more especially in Moscow and the interior of the country. In Holland the same mixture is frequently applied as a paint to outdoor woodwork, of which it is an excellent preservative. Verdigris is sometimes further applied in the preparation of other copper colours, for instance, Schweinfurt-green; also in dyeing and calico-printing; in gilding (see Gold). The neutral salt was formerly used in the preparation of acetic acid.

LEAD.

($Pb=207$; Sp. gr. $=11·37$.)

Occurrence of Lead. This metal has been known from a remote antiquity. It is only rarely found native; its chief ore is galena (PbS). It also occurs as Bournonite, or antimonial lead ore, consisting of—41·77 parts of lead; 12·76 copper; 26·01 antimony; and 19·46 sulphur; formula ($3Cu_2S,Sb_2S_3+2[3PbS,Sb_2S_3]$). From this ore copper as well as lead is extracted. The other lead ores of more or less importance are—cerusite or white lead ore ($PbCO_3$); green lead ore (pyromorphite, phosphate of oxide of lead, $3[P_2O_5,3PbO]+PbCl_2$); mimetesite (arseniate of oxide of lead, $3[As_2O_5,3PbO]+PbCl_2$); vitriol lead ore or Anglesite, sulphate of lead ($PbSO_4$); yellow lead ore (molybdanate of lead, $PbMoO_4$); and red-lead ore or krokoite, chromate of lead ($PbCrO_4$).

Method of obtaining Lead by Precipitation. Galena is the chief lead ore, 98·9 of the metal produced being extracted from it. It contains 86·57 per cent. of lead, and 13·43 per cent. of sulphur, with sometimes only mere traces, sometimes an available quantity of silver. Galena exhibits a lead-grey colour and a strong metallic lustre, crystallises in cubes, is brittle, and has a sp. gr. = 7·75. It is also employed, when finely ground, and known as Alquifoux, for the purpose of glazing coarse pottery ware; for the manufacture of Pattinson's white-lead; instead of sawdust for covering the floors of rooms in some of the German mining districts; for ornamental purposes; jewellery; and of late in a peculiar process of extracting platinum from its ores.

Lead is obtained from galena either by the precipitation method or by roasting. The former process is based upon the behaviour of metallic iron at a high temperature towards galena; for if these two substances are heated together the result is the formation of sulphuret of iron and metallic lead ($PbS + Fe = FeS + Pb$). Accordingly, the precipitation method consists in smelting the galena, previously freed from gangue, with granulated iron obtained by pouring molten cast-iron in a thin stream into cold water. The operation is carried on in a shaft furnace; the result is the formation of metallic lead, and of a lead matte consisting essentially of sulphuret of iron, undecomposed galena, and sulphuret of copper. Sometimes iron ores and slags of ironworks are applied, in which case the oxygen of these substances aids the desulphuration.

The furnace in use for the smelting is represented in figures 25, 26, and 27. B is the shaft; C, D, the hearth and crucible, which, as exhibited by the cut, is partly outside the furnace. By means of a channel the molten metal can be run off from D into the tap crucible. The gases and vapours previous to their escape into the chimney, T, are made to pass through the flues, as indicated by the arrows, in order that any solid particles containing lead, which the blast at O might carry off, may be arrested. The ore and iron, previously washed, are placed in alternate layers in the furnace. The products of the smelting collected in D, are lead, containing silver and lead matte, the latter containing about 30 lbs. of lead to the cwt., the former sometimes 3 lbs. of silver to the same quantity, while copper also may be present. This lead matte is, according to its constituents, either worked up for cementation-copper, or added to other slags containing lead and again smelted.

FIG. 25.

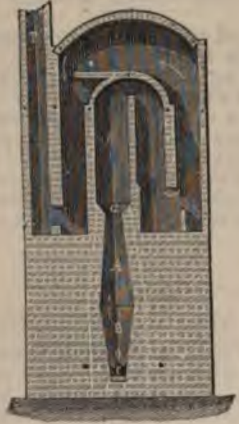


FIG. 26.

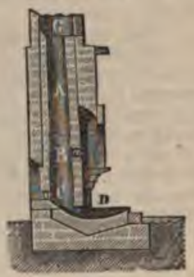
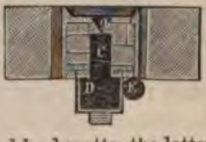


FIG. 27.

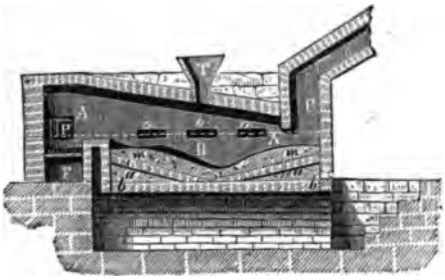


Obtaining Lead by Calcination. This process is based upon the behaviour of oxide of lead and the sulphate of that oxide towards galena, and is effected on a large scale in a reverberatory furnace. By the action of the oxygen of the air at a high temperature upon galena, a portion of this mineral is converted into oxide of lead and sulphurous acid, while sulphate of lead is simultaneously formed. By the oxygen of the sulphate and of the oxide the sulphur of any undecomposed galena is oxidised and removed ($3PbO + PbS = 4Pb + SO_2 + O$; $PbSO_4 + PbS = 2Pb + 2SO_2$). If there is present during the roasting any excess of galena, there is formed a subsulphide of lead

(Pb_2S), from which a small quantity of metallic lead is obtained by liquation, while the residue becomes a higher sulphuret ($2Pb_2S = 2PbS + 2Pb$).

The English process of lead smelting by roasting and liquation is based upon the reaction just described, and is carried on in a furnace exhibited in Fig. 28. The hearth, constructed of slag and built upon a massive wall, is arranged to slope in all directions towards the tap-hole, through which the lead runs off into a cast-iron pan set in a niche. The figures *o*, *o*, *o*, indicate the openings for the doors, three on each side of the building. T is a funnel through which the ores are placed on the hearth. Every six or seven hours a charge of 16 cwts. of ore is worked off, while the consumption of fuel amounts to about half that weight in the same time. Care is taken to spread the ore uniformly over the hearth; this having been done, the heat is gradually increased, the doors of the furnace being closed. After a lapse of two hours the doors are opened sufficiently to ventilate the furnace and dissipate the smoke, and are again closed, and the heat increased until the mass, from which lead everywhere exudes and runs off to the lowest level, becomes by stirring and the addition of fluor-spar, almost perfectly fluid. This point having been reached, the upper layer of slag is run off, at once cooled with water, and thus solidified. This slag is termed white slag from its white or light grey colour, and contains about 22 per cent. of sulphate of lead. Some small coal is now cast into the hearth in order to solidify the tough, pasty slag which covers the lead, after which the tap-hole is opened and the raw lead run off into the iron pan, previously heated so as to keep the metal in a molten state.

FIG. 28.



Raw Lead. The metallic lead obtained as described is by no means pure, usually containing silver, copper, antimony, arsenic, and other metals according to the purity of the ore. The separation of the silver, when in sufficient quantity to repay the expense of extraction, will be spoken of under Silver; but one of the by-products of some of the methods of extracting that metal is litharge, oxide of lead, which is either brought into commerce as such or reduced again to metallic lead by a process here described.

Revivification of Litharge. This process is pursued in a reverberatory furnace by placing on the hearth a mixture of litharge and small coal. The lead resulting, known as hard lead, in contradistinction to the soft lead obtained from refined litharge, is usually not quite pure. In order to give some idea of the composition of the various kinds of lead as obtained at Freiberg, Germany, we quote the following results of analyses by Dr. Reich:—

				Antimonial lead.	
	Raw lead.	Refined lead.	Hard lead.	Mülden.	Halsbrück.
Lead . . .	97·72	99·28	87·60	90·76	87·60
Arsenic . .	1·36	0·16	7·90	1·28	0.40
Antimony .	0.72	traces	2.80	7·31	11·60
Iron . . .	0·07	0·05	traces	0·13	traces
Copper . . .	0·25	0.25	0·40	0·35	traces
Silver . . .	0·49	0·53	—	—	—

Properties of Lead The colour and general physical properties of this metal are too well known to require detailed notice. Lead assumes a crystalline form with difficulty, but it is obtained in that state in a combination of cubes and octahedra by some metallurgical processes, *e. g.*, Pattinson's method of silver extraction. Lead is, when refined, a very soft and tractable metal; its absolute cohesive strength is small. When freshly cut it exhibits a strong metallic lustre, but tarnishes rapidly on exposure to air. If handled it dirties the skin, and gives, when rubbed on paper, linen, or cotton, a plumbago-coloured mark. Its sp. gr. is 11·37; 1 cubic foot weighs about 600 lbs.; 1 cubic metre, 11,370 kilos. In addition to the metallic impurities usually present in lead and already alluded to, some of its oxide is commonly mechanically mixed with it, impairing its malleability and ductility, but, on the other hand, increasing its resistance to pressure. Lead belongs to the most readily fusible metals, fusing far below red heat, at 332°; on cooling it contracts and assumes a concave surface. Lead is volatilised and boils at a strong white heat, air being excluded. It is not well suited for being worked with files or cold chisels, the former becoming clogged, and the latter blunt. Sheet lead is cut with knives of well-tempered steel. This metal does not take up more than about 1·5 per cent. of zinc; 0·07 per cent. of iron, and rather more copper, but alloys readily with tin, bismuth, and antimony.

Applications of Metallic Lead. Lead is employed in a variety of ways in building. It is much used for the leaden chambers of sulphuric acid works, and for this purpose should be as free as possible from any impurities or foreign metals, all of which impair the resistance of the sheets of lead to the acid vapours, and cause the metal to become gradually perforated with holes and cracks. The metal is further employed for leaden pans and other apparatus in chemical manufactories, for gas- and water-pipes, for rifle balls, and for many other purposes too numerous to be here specified.

Manufacture of Shot. This manufacture consists of five distinct operations, viz.—(1) the melting of the lead; (2) the granulation of the molten metal; (3) the sorting of the grain of various sizes; (4) separation of irregularly-shaped shot; and (5) the polishing of the shot. Lead intended for this manufacture is never required to be pure, and arsenic is purposely added, because experience has taught that this addition improves the spherical shape of the shot. The quantity of arsenic depends upon the quality of the lead, but varies from 0·3 to 0·8 per cent.: too much causes an irregular shape, and too little has the same defect. The arsenic is added either as arsenious acid, in which case the lead is melted under a layer of powdered charcoal, or metallic arsenic wrapped in a piece of paper is introduced under the surface of the molten lead by means of a suitable pair of forceps. The granulation of the lead is obtained by the use of a shallow sieve-like iron vessel, technically termed a card, provided with holes of regular size. The dross and scrapings from former smeltings are not removed, as they prevent the lead running too readily through the holes. The operation of granulation is carried on in shot towers, the card with the molten lead being at the top, the metal assuming a spherical shape while falling. The small spheres or drops are collected in water, to every 100 parts of which 0·025 parts of sulphide of sodium is added in order to coat the metal with a small quantity of sulphide of lead and prevent its oxidation. Shot is also made on an entirely different plan embodying the application of centrifugal force. The molten metal is forced with great speed through openings in a centrifugal machine, making 1000 revolutions per minute, the shot or particles assuming a spherical shape by reason of the great force of impact with the air near the machine. The sorting of the shot is effected by variously-sized sieves, and the separation of the imperfectly-shaped grains is obtained by causing the shot to run over a long slightly sloping table provided with ledges of wood to prevent the shot falling off sideways. Only the perfectly spherical grains of shot reach the lower end of the table. Lastly, the shot is polished by placing 100,000 parts by weight of shot and 6 parts by weight of graphite together in a cylindrical iron vessel made to rotate slowly on a horizontal axis. In this country some manufacturers prefer to use an amalgam of tin, or simply mercury, instead of graphite, for polishing. The loss of lead in the manufacture of shot amounts to about 2 per cent. The sizes and trade names of the several kinds of shot vary in different countries; in Germany No. 0 is the largest and No. 10 the smallest size.

Alloys of Lead. The following alloys of lead in daily use are made on a large scale:—Soft lead solder as used by tinsmiths, equal parts of lead and tin; the alloy used for organ pipes, usually 96 parts of lead and 4 of tin, but often more tin is added; white metal alloy for domestic utensils, as coffee and teapots, consists of lead, antimony, and tin; alloy for ships' nails, 3 parts tin, 2 parts lead, 1 part antimony. The lead used by the Chinese for lining tea-chests consists of 126 parts lead, 17·5 parts tin, 1·25 parts copper, with a trace of zinc. Other alloys, such as type metal, will be spoken of presently.

PREPARATIONS OF LEAD.

Oxide of Lead. This substance is commercially employed in two different forms, viz., as massicot or as litharge.

Massicot. Massicot, or yellow oxide of lead, occurs as a yellow or ruddy-coloured powder, obtained either by heating carbonate or nitrate of lead, or by calcining metallic lead on the hearth of a reverberatory furnace. Before chromate of lead was known, massicot was used as a yellow pigment. At red heat this substance fuses and becomes glassy. In most instances it is not a pure oxide of lead, but mixed with silicate of lead, the fact being that oxide of lead at a red heat strongly attacks any material containing silica, dissolving the silica and combining with it.

Litharge. Litharge is a fused crystalline oxide of lead, and is obtained as a by-product of the separation of silver from lead in the process to be fully described under Silver. Litharge always contains a larger or smaller quantity of oxide of copper, oxide of antimony, traces of oxide of silver, and, according to Dr. Wittstein, metallic lead, varying in quantity from 1·25 to 3·10 per cent. The oxide of copper can be removed by digesting the litharge with a solution, cold of course, of carbonate of ammonia. Litharge absorbs carbonic acid from the atmosphere, combines at a higher temperature with silica, forming with it a readily fusible glass, is soluble in acetic and nitric, and also in very dilute hydrochloric acids, and is equally soluble in boiling solutions of caustic potassa and soda. It is insoluble in carbonate of ammonia and in the carbonates of potassa and soda. Litharge is largely used, entering into various compounds for glass, so-called crystal-glass, flint-glass, strass for imitating jewels, for glazing pottery and earthenware, as a flux in glass and porcelain staining, for the preparation of boiled linseed and poppy-seed oil, for the preparations of lead-plaster, putty, minium, red-lead, and acetate of lead. A solution of oxide of lead in caustic soda lye is applied in the preparation of stannate of soda; this solution is also used for imparting to combs and other toilet articles made of horn the appearance of tortoise-shell or of buffalo-horn. A very dilute solution is used as a hair-dye, and again in metallochromy to produce iridescent colours on brass and bronze.

Minium. Red-Lead. Red-lead is a combination of oxide of lead with a superoxide, the formula being Pb_3O_4. Red-lead of excellent quality is largely manufactured near Newcastle-on-Tyne, by carefully heating oxide of lead in a reverberatory furnace expressly built for that purpose, the access of air being limited so as to prevent the fusion of that portion of the oxide which cannot then be converted into minium. Sometimes metallic lead is oxidised in a reverberatory furnace, the process, as, for instance, at Shrewsbury, being so arranged that at the hotter places of the furnace massicot, and at the cooler red-lead, is produced. The finest coloured minium, or Paris-red, is obtained from carbonate of lead by the same method. According to Mr. Burton's plan, sulphate of lead is heated with Chili saltpetre, and after the mass has been exhausted with water the red-lead is left, while sulphate and nitrite of soda are dissolved. Red-lead is used for a variety of purposes, many similar to the applications of oxide of lead. Besides being applied as a cement, when mixed with linseed-oil and mastic, for the flanges of steam-pipes, it chiefly enters the market as a pigment, being for that purpose either mixed with water or with linseed-oil. in both instances covering extremely well.

Superoxide of Lead. When red-lead is treated with moderately strong nitric acid, there are formed nitrate of prótoxide of lead and superoxide of that metal, PbO_2, a brown-coloured powder largely used in the composition of the phosphorus mixture for lucifer matches. The mixture known in lucifer match works as oxidised minium, is a dried composition, consisting of nitrate of protoxide of lead, superoxide of lead, and undecomposed red-lead, and obtained by drying a magma of minium and nitric acid.

Combinations of Oxide of Lead. Among the salts of lead employed industrially, the following are the most important:—

Acetate of Lead. This salt,

$$\left(\begin{matrix}(C_2H_3O_2)\\ Pb\end{matrix}\right\} O_2 + 3H_2O\Bigg)$$

consists in 100 parts of:—Oxide of lead, 58·71; acetic acid, 27·08; water, 14·21. It crystallises in four-sided columnar figures; is soluble in 1·66 parts of water and 8 parts of alcohol. When submitted to dry distillation it yields neutral carbonate of lead and aceton, which volatilises. When heated with sulphuric acid it yields acetic acid, sulphate of lead remaining in the retort. Acetate of lead is prepared by heating litharge or massicot with rectified vinegar, or with wood vinegar, in leaden or in tinned copper pans. The clear liquid is decanted and evaporated, and then left to crystallise in porcelain basins or in wooden tubs: 100 parts of litharge yield 150 of acetate of lead. This salt is largely used in dyeing and calico printing, in obtaining red liquor or acetate of alumina; and for the preparation of varnishes, white-lead, and chrome-yellow. We shall speak of sub-acetate of lead, tribasic acetate of lead, when considering the manufacture of white-lead.

Chromate of Lead. The basis of chromate of lead, and indeed the substance from which all chromium preparations are derived, is the chrome-iron ore, consisting mainly of protoxide of iron and oxide of chromium (FeO,Cr_2O_3, or Cr_2FeO_4). It is a magnetic iron ore$_4$ isomeric sesqui-, or per-oxide of chromium having been substituted for the peroxide of iron, but the mineral varies in composition, often containing considerable quantities of aluminia, magnesia, and protoxide of chromium. It is met with interspersed through very hard metamorphic rocks in some parts of Scotland, in colour a steel-grey or pitchy black. Its value for industrial purposes depends upon the quantity of oxide of chromium it contains; and according to M. Clouet's analysis (1869) the following chrome-iron ores contained the quoted quantities per cent. of chromic oxide:—

Chrome-iron	from	Baltimore	45
,,	,,	Norway	40
,,	,,	France	37—51
,,	,,	Asia Minor	53
,,	,,	Hungary	31
,,	,,	Oural (Russia)	49.5
,,	,,	California	42·5

Neutral, or Yellow Chromate of Potassa. This salt,

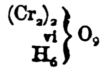
$$\left.\begin{matrix}CrO_2\\ K_2\end{matrix}\right\} O_2, \text{ or } K_2CrO_4,$$

is prepared by heating chrome-iron ore, previously pulverised and cleansed, with carbonate and nitrate of potassa on the hearth of a reverberatory furnace. The oxygen of the saltpetre cause the higher oxidation of the protoxide of iron and sesquioxide of chromium, the latter being converted into chromic acid. The thoroughly sintered, not molten, mass, is, after cooling, again ground up and lixiviated with boiling water, and also boiled for a time to extract the neutral chromate of potassa. Wood vinegar is added to the solution to precipitate the alumina and silica, after which the clear liquid is evaporated, until a film of saline material begins to form, when it is left to crystallise. The crystals take a column-like form, and are of a lemon-yellow colour, readily soluble in water, but insoluble in alcohol, and having a great tendency to become converted into bichromate or red chromate of potassa. This conversion of the neutral salt into the bi-, or acid salt, is at once effected by the addition to its solution of sulphuric or nitric acid. The bichromate of potassa or acid chromate, $K_2Cr_2O_7$, crystallises in anhydrous, aurora-red coloured prismatic crystals, soluble in 10 parts of water. This solution is highly caustic and poisonous. When heated to redness the salt gives off oxygen, leaving oxide of chromium and neutral chromate of potassa in the retort; the bichromate is prepared from the neutral salt by the addition to its solution of either sulphuric or nitric acid, preferably the latter on account of the formation of nitrate of potassa, which may be either sold or used in the manufacture of the neutral chromate.

M. Jacquelain proposes that the chrome-iron should be mixed with chalk, and the mixture heated and frequently stirred, then cooled, pulverised, and put into water, with the addition of enough sulphuric acid to produce a weak reaction, the result being the formation, first of chromate of lime, which, by the addition of the acid, becomes the bichromate of that base. The sulphate of protoxide of iron present in this solution is precipitated by means of chalk. In order to convert the bichromate of lime into the corresponding potassium salt, it is only necessary to add a solution of carbonate of potassa, the result being of course the precipitation of carbonate of lime, and the exchange of the chromic acid from the lime to the potassa. According to Tilghmann's process chrome-iron ore is mixed with 2 parts of lime, 2 of sulphate of potassa, and heated for eighteen to twenty hours in a reverberatory furnace. The same inventor suggests the heating of chrome-iron ore with powdered feldspar and lime. Mr. Swindells ignites chrome ore with equal parts of either chloride of sodium or chloride of potassium to the highest possible white heat, at the same time exposing the mixture to a constant current of superheated steam, the formation of sodium or potassium chromate resulting. The most important improvement in the preparation of chromate of potassa is the substitution of carbonate of potassa for nitrate of potassa, and the use of a furnace so constructed as to admit of the proper access of air to the strongly heated mass, the oxygen of the air being made to oxidise the chromic oxide to chromic acid. Another improvement is, that in using lime instead of alkali, the oxidation of the chromic oxide is greatly accelerated, by reason that when lime is employed instead of potassa, the heated materials do not become semi-fused or pasty, but remaining pulverulent admit of the readier access of air, as well as preventing the sinking, on account of higher specific gravity, of a portion of the chrome ore to the bottom of the hearth, and there becoming withdrawn from the action of the heat.

Applications of the Chromates of Potassa.

Before the year 1820, the salts spoken of were only used for the preparation of chrome-yellow; it was then a very expensive process, viz., the calcination of the chrome-iron ore with nitrate of potassa only. At this date, M. Kœchlin discovered the applicability of bichromate of potassa to the obtaining of what is technically termed "discharge" for Turkey-red—a madder colour—a discovery soon followed by others bearing upon the useful applications of this salt, among which are the formation of chrome-yellow and chrome-orange in calico-printing, the chrome-black in dyeing, the oxidation of catechu and Berlin-blue, the discharge of indigo-blue, the bleaching of palm-oil and other fatty substances, the preparation of mixtures for the heads of lucifer-matches, the preparation of chromate of protoxide of mercury and chromic oxide as green-coloured pigments in glass and china painting, and for the preparation of Vert Guignet, a peculiar hydrated oxide of chromium :—



$$\left.\begin{matrix}\overset{\text{vi}}{(Cr_2)_2}\\ H_6\end{matrix}\right\}O_9$$

obtained by heating 1 part of bichromate of potassa and 3 parts of crystallised boric acid, and used as a pigment in calico-printing. As might be expected, all these discoveries gave a strong impulse to the manufacture of the chromates of potassa, which have recently found still further useful applications in the obtaining of colours from coal-tar, in the manufacture of chlorine gas, in defuseling brandy and other spirits, and in the purification of wood-vinegar made from the crude pyroligneous acid.

According to M. J. Persoz, there exist, America excepted, only six manufactories of the chromates of potassa, viz., two in Scotland, one in France, one at Trjöndhem, Norway, and one at Kazan, near the Oural, Russia; the total production of these works amounted in 1869 to 60,000 cwts.

Chrome-Yellow, or Chromate of Lead. There are in technical use three different compounds of lead and chromic acid, viz., neutral chromate of lead or chrome-yellow, basic chromate or chrome-red, and a mixture of these two salts constituting chrome-orange. The first of these substances is obtained by two methods:—(1) By the precipitation of a solution of chromate of potassa with a solution of acetate of lead; or (2) by the use of sulphate or chloride of lead. According to the first plan, the operation begins with the preparation of a solution of lead, for which purpose granulated lead is put into wooden tubs placed one above the other, and the taps each tub is provided with being turned off, vinegar is poured into the upper tub. In about ten minutes the tap at the bottom of the tub is opened, and the contents let into the second tub. The operation is repeated with all the tubs, four to eight in number, the object simply being to moisten the lead thoroughly with the vinegar, so as to cause rapid oxidation on its subsequent exposure to air. The metal soon becomes coated with a bluish-white coloured film, and when this is apparent, vinegar is again poured into the topmost tub and left for about an hour, after which it is run off into the second tub, and the operation continued until there is obtained a saturated solution of basic acetate of lead. To prepare chrome-yellow, enough vinegar is added to obtain a reaction, and the fluid left to deposit any suspended sediment. At the same time, in another tub, a solution of 25 kilos. of bichromate of potassa in 500 litres of water is kept in readiness. The clear lead solution is next poured into the bichromate solution as long as any precipitate ensues. This precipitate is well washed, and usually mixed with gypsum, or sulphate of baryta, to obtain the lighter chrome colours; finally it is dried. According to Liebig, chrome-yellow is obtained from sulphate of lead, an almost useless by-product from calico-printing- and dye-works, by digesting it with a warm solution of neutral chromate of potassa. The depth of colour of the ensuing yellow pigment depends upon the quantity of sulphate of lead which is converted into chromate of lead.

Dr. Habich states that there exist two binary compounds of chromate and sulphate of lead, the formulæ of which are:—$PbSO_4 + PbCrO_4$ and $2PbSO_4 + PbCrO_4$. The former is obtained when a solution of bichromate of potassa, previously mixed with enough sulphuric acid to cause its dissociation, is precipitated with a solution of lead; while the second compound is formed if the quantity of sulphuric acid is doubled. According to M. Anthon a beautiful chrome-yellow is obtained by the digestion of 100 parts of freshly precipitated chloride of lead with 47 parts of bichromate of potassium.

Chrome-Red. The basic chromate of lead, known as chrome-red and Austrian-cinnabar, $PbCrO_4 + PbH_2O_2$,[*] is a red-coloured pigment much in demand, and obtained from the yellow or neutral chromate of lead, either by boiling it with a caustic potassa solution, or by fusing it with nitrate of potassa, the effect being that half of the chromic acid is withdrawn from the neutral chromate. Drs. Liebig and Wöhler state that chrome-red is best obtained by fusing together, at a very low red-heat, equal parts of potassium and sodium nitrates, gradually pouring into the fused salt small quantities of chemically pure yellow chromate of lead. After cooling, the insoluble chrome-red is well washed and dried. It is then a magnificently-coloured cinnabar-like crystalline powder. Professor Dulong prepares chrome-red by precipitating a solution of acetate of lead with a solution of chromate of potassa to which caustic potassa has been added. The various shades and qualities of chrome-red, from the deepest vermillion to the palest red, are caused by the difference in size of the constituent crystalline particles. This fact is proved by experiment, for when several samples are uniformly ground to a fine powder the result is the production of a uniformly deep-coloured hue. In preparing chrome-red of a deep colour, everything which might interfere with or injure the crystallisation has to be avoided. The pigments commercially known as the chrome-orange colours are mixtures, in varying proportions, of the basic and neutral chromates of lead, and are usually made by boiling chrome-yellow with milk of lime. M. Anthon recommends for the preparation of a good chrome-orange the treatment of 100 parts of chrome-yellow with 55 parts of chromate of potassa and 12—18 parts of caustic-lime made into milk of lime.

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[*] According to Dr. Duflos, see "Handbuch der Angewandten Pharmaceutisch-Technisch Chemische Analyse, &c." Breslau, 1871, p. 293, the formula of this substance is $2PbO,CrO_3$, and the dried salt does not contain any water as a component part.

Chrome-Oxide, or Chrome-Green. This substance, Cr_2O_3, is used in glass- and porcelain-staining as a *couleur grand feu*, that is to say, it stands the most intense heat provided no reducing materials are allowed to affect it. It is commercially known under the name of chrome-green as an indelible pigment for printing, being especially employed for bank-notes. It is prepared in various ways, the finest being obtained by heating chromate of protoxide of mercury, but this method is far too expensive to admit of any extensive application. Dr. Lassaigne heats equal molecules of sulphur and yellow chromate of potassa, and exhausts the mixture with water, leaving the insoluble green sesquioxide behind. Professor Wöhler prefers to mix the yellow chromate of potassa with sal-ammoniac, to heat that mixture, and afterwards treat it with water, leaving the insoluble chrome-green as a fine powder.

Among other methods of preparing the anhydrous sesquioxide is the heating of an intimate mixture of bichromate of potassa and charcoal. The hydrated oxide of chromium, according to the formula $Cr_4H_6O_9$, is met with in the trade under a variety of names, and often contains boric or phosphoric acids, not, however, as an essential constituent (See Dr. P. Schützenberger's formula on p. 65 for Guignet's-green), but as a remnant of imperfect preparation. This hydrated oxide, the preparation of which to ensure a good colour is rather a difficult matter, requiring very careful manipulation, is known as Emerald-green, Pannetier-green, Matthieu-Plessy-green, and Arnaudon-green. The pigment is used as an artist's colour and in calico-printing as a substitute for Schweinfurt-green, but is very expensive.

Chrome-Alum. This salt, $\left.\begin{matrix}Cr_2\\K_2\end{matrix}\right\}4SO_4+24H_2O$, is obtained in rather large quantities as a by-product of the manufacture of aniline-violet, aniline-green, and anthracene-red. It is a deep violet-coloured, octahedrically crystallised substance, now used to some extent as a mordant in dyeing, for rendering gum and glue insoluble, for waterproofing woollen fabrics, and for the preparation of chromate of potassa.

Chromic Chloride. This compound, Cr_2Cl_6, best prepared by the decomposition of sulphuret of chromium by means of chlorine, constitutes a crystalline violet-coloured mica-like material, employed in the manufacture of coloured paper and paper-hangings.

White-Lead. This very important preparation obtained from lead is the basic carbonate of the oxide of that metal, its formula being,

$$PbOCO_2 + x\frac{(PbOHO)}{x}$$

According to the method employed, white-lead is commercially known as of Holland or Dutch, French or English manufacture. The Dutch mode of making white-lead is founded on the fact that when metallic lead comes in contact with the vapours of acetic acid, carbonic acid, and oxygen, at a sufficiently high temperature, the metal is converted into basic carbonate of the oxide of lead. It is quite evident from this brief statement that the chief conditions being fulfilled, the methods of operation may be more or less varied. In Holland, Belgium, and some parts of Germany, the lead—as pure as possible and free from silver, which, even in small quantities greatly impairs the good colour of the white-lead—is cast into thin strips, which are wound in a spiral and placed in coarse earthenware pots. (Fig. 29.) Common vinegar is poured into the lower part of these pots, some beer-yeast being added. The lead is then placed on a perforated piece of wood, so as to prevent direct contact with the vinegar. After this the pots are covered with leaden-plates and buried (see Fig. 30) in a mass of horse-dung or spent-tan and dung. The fermentation of the dung causes the requisite increase of temperature, and the vinegar evaporating, aided by the oxygen of the air, converts the lead into basic acetate, which in its turn is converted into basic carbonate of lead by the carbonic acid resulting from the fermenting manure. This rather clumsy process has given place in Germany to the chamber method, consisting essentially in the following arrangement. Instead of the pots being made the receptacles for the lead, the strips of that metal are bent and suspended on a series of laths run lengthwise through the chamber, on the floor of which is placed a layer of spent tan, marc of grapes, or other fermentable material, saturated with vinegar. An improvement upon this arrangement is to have the chamber constructed with a double flooring, one water-tight, the other a light planking perforated so as to admit of the vapours of vinegar being carried into the compartment. The action upon the lead is in each case the same; it is converted chiefly into white-lead, and this crude product is purified from any adhering acetate of lead by washing with water before being brought into the market. There is still in use in this country a modification of the method practised by the Dutch, who, by-the-bye, are not the inventors of white-lead manufacture, the true origin being Saracenic, the trade being successfully carried on by these semi-savages in Southern Spain, whence the Dutch brought over the art in the sixteenth century to Holland. This modification consists in the following arrangement:—Granulated lead is first moistened with about 1·5 per cent. of vinegar, the metal being previously placed on hurdles in a wooden box, the interior of which is heated by means of steam to 35°, some steam being introduced to keep the lead moist. If care is taken to supply carbonic acid, after from ten to fourteen days the operation is finished, and the product having been lixiviated with water and dried, is ready for use.

Fig. 29.

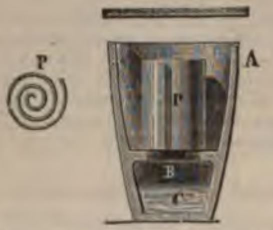
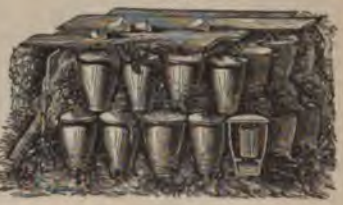


Fig. 30.



English Method of Manufacturing White-Lead. According to this plan the metal is melted in a large iron cauldron, and then made to flow on the hearth of a reverberatory furnace so as to convert the lead, by proper access of air, into litharge, which is obtained in a very finely divided state by a peculiar arrangement of the furnace. The hearth is constructed with a gutter, into which the fusing mass flows; and the sides or walls of the gutter are perforated to admit of the passage of the molten litharge, while the heavier metal sinks to the bottom. The litharge is next mixed with 1-100th of its weight of a solution of acetate of lead, and then placed in a series of closed troughs communicating with each other and admitting of the passage of a current of impure carbonic acid, obtained by the combustion of coke in a furnace provided with a blast to give an impulse to the gas. The litharge is continually stirred by machinery to accelerate the absorption of the carbonic acid gas. White-lead made by this process covers very well, and is preferred to that prepared by the wet method. We may mention in passing that it is the custom in this country to bring white-lead into the market ground with linseed oil to a thick paste, packed in strong oaken kegs or iron canisters.

French Method of Preparing White-Lead. This method, invented by MM. Thénard the elder, and Roard, is not only generally adopted in France but in all countries where it is desired to carry out a really sound and rational plan of white-lead manufacture. The method is as follows:—Litharge is dissolved in acetic acid to obtain a solution of basic acetate of lead,

$$\left.\begin{matrix}(C_2H_3O)_2\\ Pb\end{matrix}\right\} O_2 + PbH_2O_2;$$

and through the solution a current of carbonic acid gas is passed. Two molecules of oxide of lead are converted into white-lead, while neutral acetate of lead remains. Litharge is again added to the solution of this salt, and, by digestion, more subacetate of lead is obtained, which is applied as just described.

Apparatus used in White-Lead Manufacture at Clichy. The machinery and contrivances at Clichy, near Paris, for effecting the method just explained, are exhibited in Fig. 31. In the tub, A, the litharge is dissolved in acetic acid. B C is a stirrer, moved by means of the shaft shown in the engraving, bearing at the top a pulley for the strap. The solution of basic acetate of lead can be run off through the tap into the vessel E, made of copper and tinned inside, the object being to let the impurities the solution might contain subside. From E the fluid is led into the decomposition vessel constructed with 800 tubes, which pass from the top to a depth of 32 centims. beneath the level of the fluid. These tubes are in communication with the main-pipe, *gg*, which also communicates with the washing apparatus, P, answering the purpose of purifier for the carbonic acid gas generated in the small lime-kiln, G, by the ignition of a mixture of 2½ parts by bulk of chalk and 1 part by bulk of coke with sufficient access of air. The decomposition of the basic acetate of lead being finished in from twelve to fourteen hours, the supernatant liquor, neutral acetate of lead, is run off into the

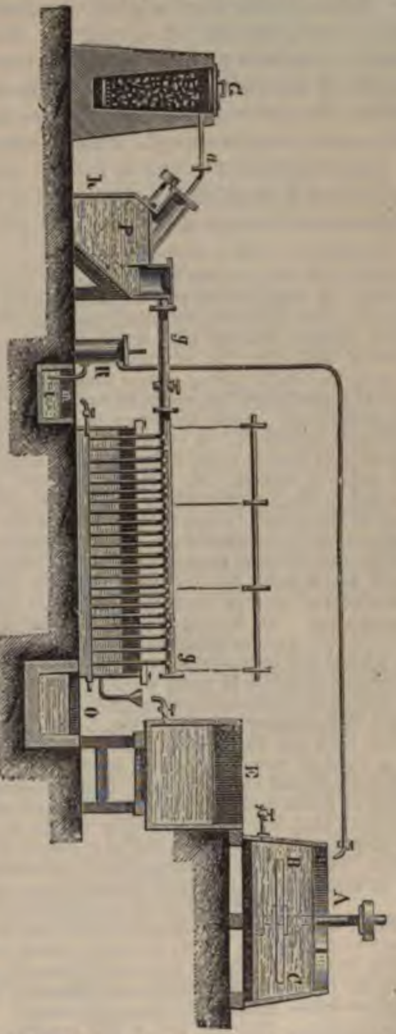


FIG. 31.

vessel, *i*, and the semi-fluid magma of white-lead passes into O. The pump, R, serves to again convey the neutral acetate to the tank, A, and the operation is re-commenced. The white-lead in O is well washed—the first wash-water being conveyed back to the tank, A—and after drying is ready for use. In order to obtain the carbonic acid cheaply, it has been proposed to ignite a mixture of chalk or limestone, charcoal, and peroxide of manganese ($CaCO_3 + C + 3MnO_2 = Mn_3O_4 + CaO + 2CO_2$.) Where admissible, the carbonic acid resulting from the fermentation of beer-wort, or of distillery-wash, may be applied. Natural sources of carbonic acid sometimes occur in the neighbourhood of active or extinct volcanoes; and near Brohl, close to the Laacher Sea in Rhenish Prussia, a locality well-known to tourists, a very plentiful and continuous supply of carbonic acid is naturally obtained and actually applied for the purpose under consideration.

Among the very various suggestions for improved methods of making white-lead, and for which an enormous number of patents have been taken out, especially in this country and in the United States, we briefly mention the following:—MM. Button and Dyer first slightly moisten litharge with water, next mix it with a small quantity of a solution of acetate of lead, place the mixture in a stone trough, agitating and passing hot carbonic acid over it. Pallu (1859) causes finely-divided lead to be thrown with great force, by means of a centrifugal machine, on an inclined plane, care being taken to moisten the lead with acetic acid. After the lapse of an hour, the finely-divided lead is converted into acetate and carbonate. A solution of acetate of lead is then poured over the mass, and the acetate of lead it contains is dissolved, while the white lead is carried into a tank, and there forms a deposit. M. Grüneberg (1860) prepares white-lead by submitting granulated lead to the simultaneous action of air, acetic, and carbonic acid, aided by the rapid motion of the metal. From private information obtained from the largest wholesale house in London, whose connections and trade relations embrace literally the whole world, dealing in white-lead, we have learned that not 1-1000th part of the *lead*, as it is technically termed, of good and saleable quality met with in the trade, is made by these new processes, since the products of most of them are deficient in some respect or other.

White-Lead from Sulphate of Lead. It is well-known that sulphate of lead ($PbSo_4$) is a by-product of various chemical operations, especially such as are carried on in connection with dyeing and calico-printing. The salt of lead thus obtained is a refuse which it has been sought to utilise in many ways. As it does not possess covering power, it cannot be used instead of white-lead as a pigment, and the difficulty of reducing it to metallic lead renders its metallurgical utilisation, if not impossible, at least highly objectionable. It has been used as a gas-purifier instead of, or in connection with, lime, and for this purpose it is a very fit material, and by becoming converted into sulphuret of lead it may be afterwards utilised as a lead ore. It is converted into white-lead by digesting it with a solution of either carbonate of ammonia or of soda. The best method for converting the sulphate of lead into metallic lead is to mix the air-dried salt with 67 per cent. of chalk, 12 to 16 per cent. of charcoal, and 37 per cent. of fluor-spar, and to smelt this mixture in a furnace. The result is the formation of carbonate of lead, which is reduced to the metallic state by carbon, the sulphate of lead and fluor-spar combining as a slag—

$$(PbSO_4 + CaCO_3 + 2C + nFl_2Ca = Pb + 3Co + CaSO_4 + nFl_2Ca).$$

According to Dr. Bolley, sulphate of lead may be reduced by the moist method by placing the salt with zinc into water, the result being the formation of chloride of zinc (*sic*) and metallic lead.* M. Krafft proposes to convert sulphate of lead into acetate of lead by boiling the former with a solution of acetate of baryta, sulphate of that base (permanent, or Chinese-white) being simultaneously formed.

Theory of Preparing White-Lead. Leaving out of the question the preparation of white-lead from sulphate of lead, the preparation of the pigment as regards all the other methods is dependent upon:—

1. The formation of basic acetate of lead;
2. The decomposition of that compound into neutral acetate of lead and white-lead. Viewing white-lead for this purpose simply as a carbonate of lead, although we shall

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* It reads in the original exactly as above translated, but whence the chlorine for the chloride of zinc is to come has been left *in nubibus*; water, sulphate of lead, and metallic zinc do not act upon each other unless some acid be present. Should dilute sulphuric be present there will be formed sulphate of zinc.

presently see that the white-lead of commerce is not so simply constituted, the formation may be illustrated by the following formulæ:—

$$\text{I.}\quad \underbrace{2\left\{\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O}_{\text{Acetic acid.}} + 3PbO = \underbrace{\left\{\begin{matrix}(C_2H_3O)_2\\Pb\end{matrix}\right\}O_2,2PbH_2O_2}_{\text{Basic acetate of lead.}};$$

$$\text{II.}\quad \underbrace{\left\{\begin{matrix}(C_2H_3O)_2\\Pb\end{matrix}\right\}O_2,2PbH_2O_2}_{\text{Basic acetate of lead.}} + 2CO_2 + \underbrace{2PbCo_3}_{\text{Carbonate of lead.}} + \underbrace{\left\{\begin{matrix}(C_2H_3O)_2\\Pb\end{matrix}\right\}O_2}_{\text{Neutral acetate of lead.}}.$$

It is therefore evident that a comparatively very small quantity of acetate of lead can produce a large quantity of white-lead, and the manufacture of that material would be endless but for the fact that white-lead retains some neutral acetate of lead, and that the loss of acetic acid cannot be practically avoided.

White-Lead from Chloride of Lead. M. Tourmentin prepares white-lead from basic chloride of lead, obtained by the action of common salt upon litharge, by mixing that compound with water, passing through it a current of carbonic acid, and next boiling the fluid in a leaden-pan with powdered chalk until a test-sample, when filtered, does not become blackened by the addition of sulphide of ammonium. The white-lead thus formed is freed from salt by washing with water.

Basic Chloride of Lead as a Substitute for White-Lead. Mr. Pattinson, of the Felling Chemical Works, near Newcastle-on-Tyne, has proposed that, instead of white-lead, a basic chloride (oxychloride) of lead should be used; and he prepares that substance by adding to a hot solution of chloride of lead ($PbCl_2$), containing from 400 to 500 grammes of the salt to the cubic foot, an equal bulk of saturated lime-water. This addition causes the throwing down of the compound ($PbCl_2 + PbH_2O_2$), which after having been collected on a filter and washed, is dried and used as a pigment. The chloride of lead is obtained directly from galena, which is decomposed from leaden-vessels with strong hydrochloric acid. The sulphuretted hydrogen thus formed is carried by suitable tubing to a burner in the sulphuric acid chamber, the resulting sulphurous acid from the combustion being used for the production of sulphuric acid. Pattinson's white-lead is not so white as ordinary white-lead, its colour verging to yellow, but this is no objection where white-lead is to be used with other paints, and the less so as Pattinson's oxychloride of lead covers well.

Properties of White-Lead. When unadulterated and well-made, white-lead is an exquisitely fine white-coloured powder, void of taste and smell. The white-lead of commerce exhibits, according to the mode of preparation, different features; one preparation is met with in flakes, having been obtained by the corrosion of thin strips of lead placed in pots. The lead known as Krems-lead is pure white-lead made in thin cakes by means of gum-water.

The variety of white-lead known as pearl-white is blued with either a small quantity of indigo or Berlin-blue. The white-lead of commerce has frequently been made the object of chemical analysis, especially by Dr. G. J. Mulder and M. Grüneberg. The results of the analyses of the under-mentioned samples prove the correctness of the formula given above. The numbers refer to:—1. Krems white-lead. 2. Precipitated by the Clichy method and manufactured at Magdeburg. 3. From the Harz. 4. Another sample from Krems. 5. A sample from a chemical laboratory by imitating the Dutch method on a limited scale. 6, 7. Samples from Klagenfurt, Carynthia. 8. English lead manufactured according to the Dutch method.

	1.	2.	3.	4.	5.	6.	7.	8.
Oxide of lead ..	83·77	85·93	86·40	86·25	84·42	86·72	86·5	86·51
Carbonic acid ..	15·06	11·89	11·53	11·37	14·45	11·28	11·3	11·26
Water	1·01	2·01	2·13	2·21	1·36	2·00	2·2	2·23

It is certain that the covering properties of white-lead are dependent upon its state of aggregation, because a loose crystalline white-lead does not cover nearly as well as the perfectly amorphous lead prepared by the old Dutch method. It appears that the covering power increases with the amount of hydrated oxide of lead. This is proved by the fact that those who merely choose white-lead by its covering power are often misled, a fact lately tested by the translator of this work, by giving to a man, thoroughly acquainted with white-lead as commercially met with, a mixture of carefully-prepared and dried hydrated oxide of lead, to which white precipitate, subnitrate of bismuth, and carbonate of bismuth had been added. The man, after testing a series of samples of purposely-adulterated white-lead, all of which he detected as adulterated, was unable to speak with certainty of the above mixture, which he took for pure lead.

Adulteration of White-Lead.

It has been, and is still, to some extent, the custom in the manufactories to add to white-lead a certain quantity of sulphate of baryta, either native or artificially prepared. Lead is often mixed with sulphate of lead, chalk, carbonate of baryta, sulphate of baryta, and pipe-clay; but these adulterations are most common in the retail trade. Not any of these substances ought to be present; they possess no covering power and needlessly absorb oil. Pure white-lead ought to be perfectly soluble in very dilute nitric acid, and in the resulting clear solution caustic potassa should not produce a precipitate, for if it does chalk is present. An insoluble residue in the dilute nitric acid indicates the presence of gypsum, heavy-spar, or sulphate of lead. The sulphate of lead may be recognised by reducing the lead with the blowpipe. Sulphate of baryta can be made evident by ignition with charcoal in the blowpipe flame, treating the residue with dilute hydrochloric acid, and adding a solution of gypsum, which again yields a precipitate of sulphate of baryta. Gypsum does not yield an insoluble precipitate with dilute nitric acid, but does so with a solution of oxalate of ammonia. According to Dr. Stein the most simple method of estimating quantitatively a mixture of white-lead and sulphate of baryta, is to heat the weighed sample in a piece of combustion-tube, and to collect the carbonic acid in a Liebig's potassa-bulb, a chloride of calcium-tube being fastened by a perforated cork to the combustion-tube to absorb the moisture. The quantity of carbonic acid given off stands in direct proportion to the quantity of carbonate of lead present. Pure white-lead of good quality gives off about 14·5 per cent. of the gas, and, according to Dr. Stein's researches, the undermentioned series of mixtures gave off the quantities of carbonic acid indicated.

33·3 parts of white-lead and 66·6 parts of heavy-spar lost by ignition 4·5—5 per cent.
66·6 " " 33·3 " " " 6·5—7 "
80·0 " " 20·0 " " " 13·0 "
50·0 " " 50·0 " " " 10—10·4 "

Applications of White-Lead.

The extensive applications of this material as a constituent of paints, "to give body," as the term runs, and as putty, and for various chemical operations, are well known. It has been experimentally proved by Dr. G. J. Mülder in his treatise "On the Chemistry of Drying Oils and the Practical Applications to be drawn therefrom," that the quantity of white-lead used in proportion to linseed-oil for painting purposes is far too great, being on an average from 250—280 parts of white-lead to 100 parts of oil, while the author found that 52 parts of unadulterated white-lead, or 44 parts of oxide of lead (PbO) to 100 parts of raw or boiled linseed-oil are amply sufficient quantities. White-lead, however useful, is very sensitive to the action of sulphuretted hydrogen, by which it is blackened and discoloured, causing not only all the white paint to be spoiled, but also all pigments and paints of which white-lead is a constituent, as may be seen to a very large extent every summer at Amsterdam, where from the stagnant canals sulphuretted hydrogen is abundantly given off. The action, however, of the sea air in autumn has the effect of somewhat restoring the blackened and discoloured painted surfaces to their primitive hue. The late Professor Thénard suggested that pictures which had become blackened should be cleaned by means of peroxide of hydrogen, the oxygen of which present as ozone converts the blackened lead colours into white sulphate of lead.

In this country it has become an almost universal custom to sell white-lead ready ground with linseed-oil into a thick paste. This practice certainly saves painters a great deal of trouble, but is also pregnant with the difficulty of detecting adulteration, while there is a chance of an inferior oil, rosin oil, being added. The oil almost entirely prevents the action of any acid upon the paste; even if very strong nitric acid be taken, and heat applied, the decomposition and disintegration are very slow and incomplete, and, besides, owing to the insolubility of nitrate of lead in nitric acid, the action of strong nitric acid upon oil thus mixed gives rise to a variety of compounds, which interfere with the usual modes of testing the white-lead. To remove the oil in order to test white-lead, the best plan is to thoroughly incorporate some of the sample with a mixture of chloroform and strong alcohol in equal parts, and to wash the mass by decantation or on a filter with a fluid composed of 2 parts of chloroform and 1 of strong alcohol. The quantity of the oil may then be ascertained by the evaporation of this solvent. After washing once or twice with boiling alcohol and then drying, the white-lead can be readily tested by any of the known methods.

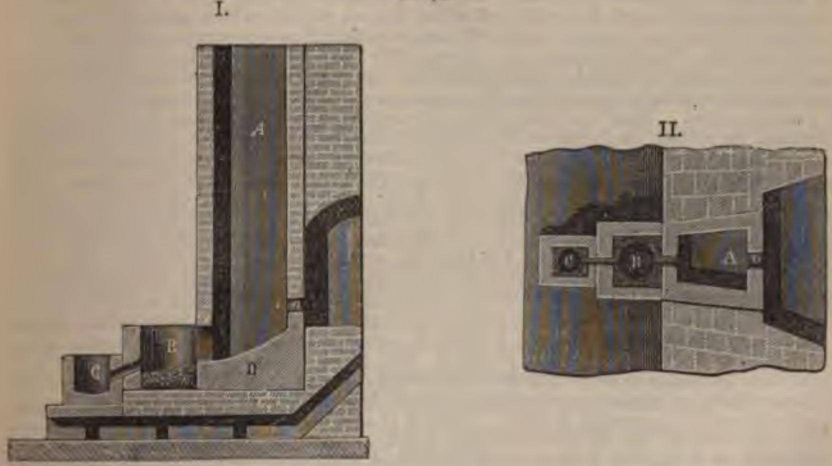
TIN.

($Sn = 118$; Sp. gr. = 7·28.)

Occurrence and mode of obtaining the Metal.

Tin does not occur naturally in a metallic state: it is found as oxide in tinstone, or tin ore, SnO_2, containing 79 per cent. of metal, and as sulphuret of tin in combination with other metallic sulphurets in tin pyrites, $(2Cu_2S + SnS_2) + 2(FeS,ZnS),SnS_2$, with 26 to 29 per cent. of tin. Tin ore occurs either interspersed in veins, in syenitic and similar rocks, or in secondary formations deposited from water, and consisting of various detritus, when it is known as *seifer*. These ores are not as a rule simply composed of pure oxide of tin, but contain various other metallic compounds, among which are sulphur, arsenic, zinc, iron, and copper. In some instances, in Cornwall, Malacca, Banca, and Billiton, tin ore is met with among the detritus of ancient river-beds in a very pure state, since the mechanical separation of the ore from impurities has been performed by nature itself, and as a consequence these ores yield a purer metal than the ore obtained from veins, which has to undergo dressing, washing with water, and roasting, previously to being smelted, in order to eliminate the arsenic, sulphur, and antimony. Tinstone occurs in Saxony in the earlier granitic formation. The ore is accompanied by, and partly mixed with, wolfram, molybdenum-glance, sulphur, and arsenical pyrites, and bears the name of Zinnzwitter. Fig 32, I. and II., represent the furnace in use at Altenberg, Saxony, for smelting the roasted tin ore. It is built of granite upon a strong foundation of gneiss, and is about three metres in height. A is the shaft, B the fore-hearth, and D the bottom-stone, consisting of one single piece of granite scooped out in the direction of B. B is in communication with the iron cauldron, C; while the tuyere of the blast is placed at B. The ore, mixed with coke, coal, or charcoal, and with slag from former smeltings, is placed in A; the reduced tin collects first on the fore-hearth, B, and runs thence into C. The metal, however, is not pure, but contains iron and arsenic. It is separated from these impurities by a process of liquation; the pure tin fusing more readily, oozes out and leaves behind an alloy of iron and tin fusible with greater difficulty. The metal thus obtained is very pure, containing hardly as much as 0·1 per cent. of foreign metals; it is known in the trade as refined

FIG. 32.


I. II.

tin. The slags, as well as the alloy remaining, are smelted separately or together for tin, and the result brought into the market as block-tin. In Bohemia and Saxony, tin is cast either in ingots or in cakes. Banca and Billiton tin, a very pure metal, is cast in slabs. If tungsten ores occur with tin ores, there is great difficulty in obtaining pure metal. Tin ore found in Cornwall—and this county has yielded tin for at least 2,000 years—has to be smelted according to the ancient Stannary laws.

Properties of Tin. Tin, as regards its colour, approaches the nearest to silver, only differing by a somewhat bluish hue, and it exhibits a high metallic lustre very similar to silver. It is, next to lead, the softest metal, yet is somewhat sonorous, for if a rod of tin be free to swing, and is gently tapped, a sound is produced; this is not the case under similar conditions with lead, thus proving tin to be considerably harder, also proved by the fact that it is not easily scratched with the nail. The bending of a rod of tin causes a creaking noise, which is the stronger the purer the tin. Tin is very malleable, and admits of being beaten to very thin foil, but it is not a very ductile metal. When rubbed between the fingers it imparts to them a peculiar odour. The sp. gr. of pure tin is 7·28, and by hammering may be increased to 7·29; a cubic foot of tin weighs, according to its purity, from 375 to 400 lbs. Tin fuses at 228°, and becomes very brittle when heated to nearly that temperature. If the metal is intended for casting—it is, however, very rarely used in a perfectly pure state for castings, as it does not fill the moulds well—its metallic lustre and degree of cohesion after cooling entirely depend upon the temperature of the tin at the time of casting. If too hot and exhibiting rainbow colours, its surface will appear striped and reddish-yellow after cooling, and the metal will be brittle if again heated to 100° to 140°; if not sufficiently heated, though in a fluid state, it is, after cooling, dull and brittle. The greatest metallic lustre is obtained, and simultaneously the greatest cohesive strength, when the surface of the metal while molten exhibits a high degree of lustre. At a white heat tin boils and volatilises, air of course being excluded; for if the metal be kept fused in contact with air, it becomes covered with a greyish coating of protoxide of tin and finely-divided metal, termed tin-ash, which substance when the heating is continued becomes converted into a yellowish-white stannic oxide, known as putty powder. Tin by exposure to air gradually loses its metallic lustre, but is by no means so readily affected by sulphuretted hydrogen and ammoniacal vapours as silver, and is used to imitate that metal in the construction of lustres for gas lamps, &c.

Applications of Tin. Now that china and earthenware have become cheap, and other alloys are used for spoons, tin is not so frequently in demand as in former times for domestic utensils. Tin, though next to silver the dearest of metals, is met with in quantities measured by the ton, which of tin varies in price from £120 to £180—copper being from £95 to £105—and is largely used both as an alloy (for those with copper see under that metal), and in a pure state for various kinds of vessels for pharmaceutical and chemical operations, for worms of distilling apparatus, for the working parts for dry and wet gas-meters, and for block-tin pipes for conveying gas and water, &c. However, for many purposes, an alloy known in this country as pewter, of lead and tin in varying proportions, is preferred, because this compound is harder and stands wear and tear better than these metals separately. An alloy of lead and tin is called abroad *two-poundly* when the metals are present in equal quantities, and *three-poundly* when consisting of 2 pounds of tin and 1 of lead. Tin, either pure or more or less alloyed with lead, may be beaten or rolled into thin sheets and foil, and applied in a great many ways; among which, one of the chief, although gradually being superseded by a process of silvering, is tinning or amalgamating mirrors. Tin-foil is also used for the packing of chocolate, soap, cheese, fruit, &c., all of which keep very well under these conditions. Commercial silver-foil or leaf-silver is an alloy of tin with a little zinc; in combination with other metals, viz. copper, antimony, and bismuth, in varying but small quantities, it constitutes a composition metal used for making teaspoons and other similar objects. Britannia metal consists of 10 parts of tin and 1 of antimony, its various applications are well known.

As the specific gravity of those metals with which tin is purposely or naturally alloyed differs, the determination of the sp. gr. is a means of estimating the purity of the metal. The undermentioned figures illustrate this in the more commonly occurring alloys of tin and lead:—

Parts Sn	+	Parts Pb	Sp. gr.	Parts Sn	+	Parts Pb	Sp. gr.
1	+	1	8·8640	1	+	4	10·183
2	+	3	9·2650	3	+	2	8·497
1	+	2	9·5530	2	+	1	8·226
2	+	5	9·7700	5	+	2	8·109
1	+	3	9·9387	3	+	1	7·994
2	+	7	10·0734				

The material known as putty-powder and calcined tin-ash is used for polishing glass and metals, and for producing white enamels.

Tinning. By this term we understand the covering of other metallic surfaces with a thin and adhesive film of tin. This operation only succeeds well when the surface of the metal to be tinned is quite free from oxide, and when during the operation the oxidation of the molten tin is prevented. The former requisite is attained by the action of dilute acids, rubbing and scouring with sand, pumice-stone, &c.; the latter condition by the use of either rosin or sal-ammoniac, both of which cause the reduction of any oxide that may be formed.

Tinning of Copper, Brass, and Malleable Iron. The vessels or other objects intended to be tinned are heated nearly to the melting-point of tin; some molten tin is then poured into the vessel, and brushed about with a piece of hemp over which some powdered sal-ammoniac is strewed. Pins, hooks and eyes, small buttons, and similar objects are tinned by being boiled in a tinned boiler filled with water, granulated tin, and some cream of tartar. The tinned objects are dried by being rubbed with sawdust or bran.

Tinned Sheet-Iron. This well-known material, from which so many useful objects are made by the tinman, is not, as is frequently supposed, rolled out sheet-tin, but tinned sheet-iron. The iron previously to being covered with tin is thoroughly scoured, so as to present a clean metallic surface, and then immersed in baths of molten tin covered with a layer of molten tallow to prevent the oxidation of the metal. On being removed from the tin-bath the sheets are immersed in a bath of molten tallow to remove any excess of tin, wiped with a brush made of hemp, next cleaned with bran, and packed. In order to obtain iron covered with an alloy less easily fusible, MM. Budy and Lammatsch add about $\frac{1}{18}$th of nickel to the tin.

Moire-Metallique. When tinned sheet-iron, technically termed tin-plate, is washed over with a mixture consisting of 3 parts of hydrochloric and 1 part of nitric acid diluted with 3 parts of water, and then cleaned with pure water, there will be observed a peculiar, somewhat mother-of-pearl-like appearance, due to the crystalline particles of tin, produced by the rapid cooling, reflecting the light unequally.

PREPARATIONS OF TIN.

Aurum Musivum; Mosaic-Gold. The substance known under that name is in reality a bisulphide of tin (SnS_2), prepared in the following manner:—4 parts of pure tin, with 2 of mercury, are amalgamated by the aid of a gentle heat, and introduced with $2\frac{1}{2}$ parts of sulphur and 2 of sal-ammoniac into a flask, and heated on a sand-bath, at first gently and then gradually increasing to a full red heat. First the sal-ammoniac volatilises, and next mercury in the shape of cinnabar mixed with a trace of the sulphide of tin; while there is left the preparation known as mosaic-gold, forming the upper layer of the remaining contents of the flask, the lower portion being a badly-coloured sulphide. The *rationale* of the formation of this peculiar coloured sulphide, that is, peculiar as regards its physical appearance, is not quite clearly explained; the compound, moreover, may be prepared without mercury. When properly prepared, it appears as a golden-coloured metallic substance, greasy to the touch, and soluble in the alkaline sulphurets. It is chiefly used for imitating gilding on painted surfaces, but its employment is very much restricted from the fact that the bronze-colours are more satisfactory in result. Indeed, in the English market, mosaic-gold is almost obsolete.

Tinsalt. By the name of tinsalt the trade understands chloride of tin ($SnCl_2$), but the commercial article, being prepared by dissolving granulated tin in hydrochloric acid and evaporating the solution, is really ($SnCl_2 + 2H_2O$). According to M. Nöllner hydrochloric acid gas should be caused to act on granulated tin placed in earthenware receivers, and the concentrated tinsalt solution thus obtained evaporated in block-tin vessels. The salt occurs in the trade in colourless, transparent, deliquescent crystals, of course very soluble in water. The aqueous solution, unless acidulated with more hydrochloric or tartaric acid, soon deposits a basic salt. Tinsalt is used chiefly in dyeing and calico-printing.

Nitrate of Tin, or Physic. Under this name dyers use a solution of refined block-tin in aqua regia, and usually this substance is a mixture of perchloride and protochloride of tin. The material known as pinksalt is a double chloride of tin and ammonium—

$$(SnCl_4 + 2NH_4Cl).$$

A concentrated aqueous solution of this salt is not decomposed by being boiled, but, when diluted, the oxide of tin is thrown down. Pure chloride of tin is used in France in the preparation of fuchsine; while as a solution it is used by M. Th. Peter, at Chemnitz, for dyeing in iodine-green.

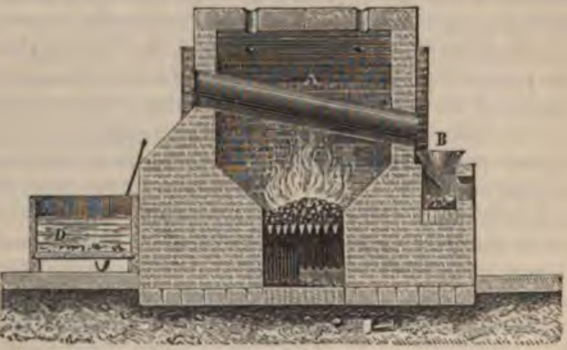
Stannate of Soda. This salt is now very largely used in dyeing as well as in calico printing, and is prepared in various ways, sometimes by fusing tin-ores with caustic-soda and lixiviating the molten mass with water; or, according to Mr. Brown, by boiling soda-lye with metallic tin and litharge, the effect being the formation of stannate of soda and metallic lead. Dr. Häffely somewhat modifies this process by digesting litharge with soda-lye at 22 per cent. in a metallic vessel. Into the solution of plumbate of soda thus obtained, granulated tin is placed and heat applied. Sometimes a stannite of soda is used and made by dissolving tinsalt in an excess of caustic soda, but this preparation is unstable, and does not answer well in dyeing and printing; it is only extemporaneously used on a limited scale by small dyers.

BISMUTH.

($Bi = 210$; Sp. gr. $= 9{\cdot}79$).

Occurrence and Mode of Obtaining. Bismuth is a rather rare metal. It occurs in Peru and Australia, chiefly native, and with cobalt and silver ores in granite-gneiss and metamorphic rocks. It is also found as oxide, the ore being known as bismuth-ochre, BiO_3, containing 89·9 per cent. metal; as sulphide, or bismuthine, BiS_3, with 80·98 per cent. metal; and as bismuth-copper ore, with 47·24 bismuth. As bismuth is chiefly found in the native metallic state, and is a readily fusible metal, its extraction from gangue is not a difficult matter, and consists in a process of liquation.

FIG. 33.



Bismuth Liquation Furnace. The contrivance in use near Schneeberg, in Saxony, for the smelting of bismuth is exhibited in Fig. 33. The ore, containing on an average from 4 to 12 per cent. metal, separated as much as possible by mechanical means from the gangue, is broken up to the size of hazel-nuts and placed in the cast-iron tube, A, heated by means of the furnace. The fluid metal runs out into B, an iron-pot kept sufficiently hot by means of charcoal to prevent the solidification of the metal, and partly filled with charcoal-powder to prevent the oxidation of the metal. The residue in the iron tube is discharged into the water which fills the box, D. By this method of liquation about two-thirds of the bismuth contained in the ore is reduced. Bismuth, as has been stated (see Cobalt), is obtained as a by-product, and from the refuse of the refining of certain silver ores, which are treated with dilute hydrochloric acid, the basic chloride of bismuth being precipitated by water, afterwards dried, and reduced by means of soda.

Properties of Bismuth. Bismuth possesses a reddish-white colour, strong metallic lustre, and crystalline texture. It is hard, but so brittle that is readily pulverised, yet with careful treatment proves to be somewhat ductile. Its fusion-point is variously given by different authors, the latest determination of pure metal in an atmosphere of hydrogen is by Dr. van Riemsdijk, who found bismuth to melt at 268·3°. On cooling bismuth expands very considerably.

α is Saxony, β Peruvian bismuth; composed in 100 parts:—α. Bismuth, 96·731; antimony, 0·625; arsenic, 0·432; copper, 1·682; sulphur, 0·530. β. Bismuth, 93·372; antimony, 4·570; copper, 2·058.

Applications of Bismuth. Bismuth in the metallic state is chiefly used for certain alloys. Its oxide enters with boric and silicic acids into the composition of some kinds of glass, and is used for porcelain- and glass-staining. The basic nitrate, or *magisterium bismuthi*, and the carbonate are used in medicine, and the former, under the name of *Blanc de fard*, is employed by ladies for painting and beautifying their faces. Among the alloys of bismuth those with lead, tin, and cadmium (see that metal), are the most important. Newton's fusible alloy is composed of bismuth, 8 parts; tin, 3; lead, 5; and melts at 94·5°. Rosse's fusible metal consists of 2 parts of bismuth, 1 of lead, 1 of tin, and fuses at 93·75. If a small quantity of cadmium be added to these alloys they are rendered still more easily fusible. An alloy composed of lead 3 parts. tin 2 parts, bismuth 5 parts, fuses at 91·66, and may be used for stereotyping purposes, but is rather expensive. This alloy is also used for making the pocket-book metallic-pencil for writing on paper prepared with bone-ash. Alloys containing bismuth were used as safety-plugs in steam-boilers; these plugs were screwed into one or more of the plates exposed to the force of the steam, usually in or near the steam-chest or dome, the idea being that the plugs would melt if the temperature of the steam rose beyond certain limits. Experience, however, has sufficiently proved that these plugs, although carefully made, did not act as a real preventative to boiler-explosions.

ZINC.

Zn = 65·2; Sp. gr. = 7·1 to 7·3)

Occurrence of Zinc. This metal, known only a comparatively short time, is never found native, but in combination with sulphur (ZnS), with 67 per cent. of metal, under the name of blende or black-jack, the ore sometimes containing traces of indium. It also occurs combined with oxygen as noble-calamine, carbonate of zinc, or zinc-spar ($ZnCO_3$), with 52 per cent. of zinc; as ordinary calamine-stone, or hydrated silicate of zinc, with 53·8 per cent of metal; as red zinc-ore or red oxide of zinc, frequently containing manganese; as Gahnite ($AlZnO_4$); and further as an admixture with other ores.

Method of Extracting Zinc. The general plan is to roast the ore and then mix it with the requisite quanty of carbonaceous matter and suitable flux, care being taken that the latter shall not give rise to the formation of any oxidising material; for instance, if the ore requires lime as flux to take up the gangue, calcined limestone, and not chalk or limestone is used. The action of the fuel is aided by a blast, best of dry air. The products of this mode of treatment are:—1. Metallic zinc, the vapours of which condense in properly constructed and cool channels. 2. Hot gases usually applied for heating steam-boilers or other purposes. 3. The non-volatile materials, gangue and flux, slag with some metal.

Distillation of Zinc in Muffles. With the exception of cadmium, zinc is the most volatile of the readily fusible metals, while its melting-point is nearly twice the number of degrees of that of tin, the most fusible of the commercially valuable metals; this property is utilised in extracting the metal from its ores. The mode of distillation varies in some particulars in the three chief zinc producing countries, Silesia, Belgium, and England. In Silesia and Germany the apparatus used for the distillation of zinc consists (see Figs. 33, 34, and 35) of a muffle-shaped fire-clay retort, the front or mouth of which is provided with two openings, the lower, *a*, being closed by a door which is opened only when the residue of the distillation is taken out. At *b*, the other opening, a rectangularly bent tube is inserted, provided with a small hole at *c*, closed by a plug when the operation of distilling is proceeding, and by which the ore is introduced into the retort. At *d* the molten zinc runs off. The muffles are placed to the number of from 10 to 20 in a furnace (see Fig. 36) constructed internally somewhat like gas-retort furnaces, and rest on what are technically termed benches. The arches of the furnaces are so constructed as to concentrate the heat from the hearths placed longitudinally. The metal is received in crucibles placed in the recesses, *tt*. As the first portion of the metal and oxide carried over contains nearly all the cadmium existing in the ore, that portion is kept separate for the purpose of extracting cadmium. At the outset of the distillation the condensation room, *t*, is so cool that the vapours of the zinc become solid without agglutination, that is, remain finely divided. This product, though of course containing oxide, frequently yields 98 per cent. of metallic zinc. Afterwards the metal carried over is what is termed drop-zinc, that is to say, the liquid runs off in a molten state. This crude zinc is refined by another smelting, and comes in the market in slabs about 2 inches thick by 10 long and 5 to 6 wide.

FIG. 34.

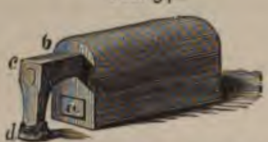


FIG. 35.

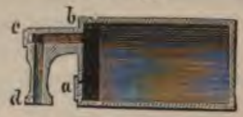
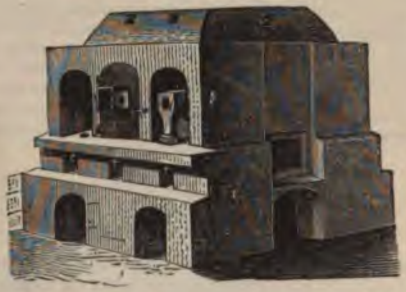


FIG. 36.



Distillation in Tubes. At the celebrated zinc-works of Vieille Montagne, near Liège, Belgium, zinc ore is distilled in tubes. These tubes are placed in rows in a slanting position; they are made of fire-clay, 1 metre in length by 18 centims. width and 5 centims. thickness (see Fig. 37), and closed at one end; the open ends are flush with the front brickwork of the furnace, in order that the charge of ore, flux, and carbonaceous matter may be introduced. Fig. 38 exhibits a cast-iron conically-shaped tube, 25 centims. long, and Fig. 39 a sheet-iron tube 20 centims. long, both of which are fastened to the fire-clay tube to receive the volatilised metal. A vertical section of the Belgian furnace used for the distillation of zinc is shown in Fig. 40, with the mode of placing the tubes, the closed ends of which rest on a projection of the brick-work. The ore is first calcined in a shaft-furnace, and the charging of the tubes usually takes place every morning at six o'clock, when the fire is rather low.

FIG. 37.

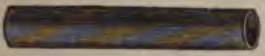


FIG. 38.

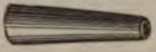


FIG. 39.

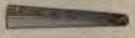
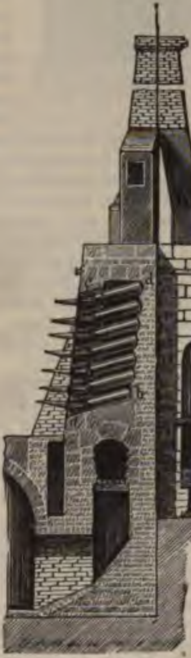


FIG. 40.

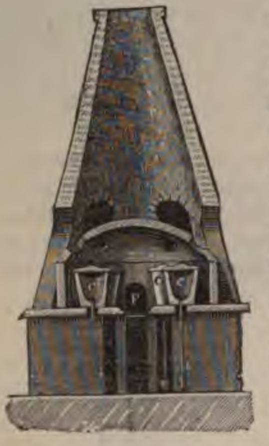


Distillation of Zinc in Crucibles. The zinc-smelting as carried on near Sheffield, Birmingham, and in Wales and other localities, is performed by downward distillation. The furnaces represented in Fig. 41 are constructed to contain six or eight fire-clay crucibles, *cc*, access to which is obtained through holes made in the fire-arch of the furnace. The bottom of each crucible is perforated and fitted with a tube to carry off the volatilised zinc; during the time of charging this tube is closed with a wooden plug, which is of course burnt during the strong ignition. At first the crucibles are left open, but as soon as a bluish flame begins to show itself, the covers are put on. The condensation-tube is then applied over a vessel containing water to prevent the spirting of the metal. The zinc is ultimately refined by smelting in iron crucibles.

Mode of Obtaining Zinc from Sulphuret of Zinc, the Black-Jack of the English Miners. There are two modes of utilising this zinc mineral. In one plan the sulphuret is first roasted so as to convert it into oxide, and then treated as before described; or the ore is directly applied by adding a quantity of iron ore sufficient to desulphurise it, lime being used as flux. The iron ore, if containing water or carbonic acid, ought to be calcined previously to being used for this purpose; but instead of iron ore metallic iron is often used. Mr. Swindells has proposed to calcine native sulphuret of zinc with common salt, the result being the formation of sulphate of soda and chloride of zinc. The mass being lixiviated with water, from which the sulphate of soda crystallises, the chloride of zinc remains in solution and is precipitated by means of lime, yielding oxide of zinc. This oxide is treated for metal in the ordinary manner.

Properties of Zinc. The colour of zinc is bluish-white or grey; its crystalline structure varies according to its purity, and according to the temperature at which it was cast and the more or less rapid cooling. When zinc is cast and rapidly cooled the specific gravity is 7·178, but when slowly cooled it is 7·145, and by hammering and laminating may be increased to 7·2 and even 7·3. A cubic foot of zinc weighs, therefore, from 360 to 390 lbs. Zinc is slightly harder than silver, but like lead and tin it is not fitted for filing, as it chokes the teeth of the files. When pure, zinc is sonorous; it is a brittle metal possessed of a very small absolute tenacity, but offers a great resistance to crushing weight, when not subjected to sudden blows. Very pure zinc may be hammered out at the ordinary temperature, but the malleability is greatest at temperatures between 100° and 150°. Zinc melts at 412° in the open air, and perfectly pure zinc melts in an atmosphere of hydrogen at 420°. According to MM. Troost and Deville zinc volatilises, air or oxygen being excluded, at 1040°, and may be distilled; when heated in contact with air to 500° zinc burns, emitting a very strong greenish blue-coloured light, and forming oxide of zinc (zinc-white), which is not volatile. Of all the metals used on a large scale, zinc has the highest coefficient of expansion by heat, its longitudinal expansion for temperatures from 0° to 100°, being for cast zinc $\frac{1}{340}$, for sheet zinc $\frac{1}{322}$, consequently molten zinc greatly contracts while cooling. The malleability, tenacity, and cohesive force of zinc are greatly impaired by temperatures ranging from 150° to 200°, at which zinc may be pulverised. Superheated steam oxidises zinc ($H_2O + Zn = ZnO + H_2$), and this property is made use of in the separation of this metal from lead. When exposed to a moist atmosphere zinc is superficially oxidised, but as the oxide adheres strongly to the metal further corrosion is prevented. Zinc is so readily oxidised and acted upon by water, weak acids, and alkalies, that it is not at all a suitable metal for vessels intended to hold potable liquids or moist solids, as these substances take up zinc and become poisonous. An addition of 0·5 per cent. of lead renders zinc far more malleable; but if the zinc is to be used for the preparation of brass, even 0·25 per cent. of lead is injurious, and for brass-making zinc containing lead is avoided. Zinc often contains some 0·3 per cent. of iron, but this does not impair the good quality; the iron is usually derived from the iron pots used for re-melting the crude metal; if, however, the quantity of iron increases the zinc becomes brittle and cracks. Zinc obtained from calamine is usually purer than that obtained from the native sulphuret. The black residue remaining when zinc is dissolved in acids; and often mistaken for a carburet of zinc, is a mixture in various proportions of iron, lead, and carbon. The more impure the zinc, the more readily it is dissolved in acids, but by careful distillation zinc may be almost entirely freed from any foreign metals. In contact with iron zinc prevents the oxidation of that metal. Zinc precipitates copper, silver, lead, cadmium, arsenic, antimony, and others from their solutions.

FIG. 41.



Applications of Zinc. This metal is very largely used for covering roofs, making water-spouts, tanks for holding water, and for various architectural purposes. It should be borne in mind that for roofing purposes zinc is in so far dangerous as to greatly increase the intensity of fire should buildings covered with zinc become ignited; one instance of this danger was exhibited in March, 1866, when the huge wooden building then standing in Lower Kennington-lane, and used as a floor-cloth factory, caught fire, the burning of the sheets of zinc covering the roof producing a heat so intense as to ignite no less than sixteen adjacent houses, although these were from 20 to 30 yards from the burning shed. Zinc is used in galvanic batteries, in various alloys, in chemical laboratories, and for galvanising iron wires, as well as for the preparation of zinc-white, and for various ornamental castings, which are made in iron moulds previously thoroughly heated to prevent a too rapid cooling and contraction of the metal. The Prussians make use of zinc for cartridges. The total annual production in Europe of this metal amounted (1870) to 2,154,000 cwts., of which England produces 150,000 cwts.; in the metropolis, Vieille Montagne (Belgium) zinc is almost exclusively used.

PREPARATIONS OF ZINC.

Zinc-White. Under this name there has during the last fourteen years been brought into the market anhydrous white oxide of zinc, applied instead of white-lead as a pigment. Zinc-white is prepared for this purpose by oxidising metallic zinc in fire-clay retorts, placed to the number of 8 to 18, in a reverberatory furnace. As soon as these retorts are at a bright white-heat, cakes of zinc are placed in them, and the vapours of the metal on leaving the retort are brought into contact with a current of air heated to 300°; oxidation results, and the oxide, a very loose, snow-white, flocculent material, is carried by the current of hot air into condensing chambers, and gradually deposited. The oxide thus prepared is immediately fit for use; it is of a pure white colour, and very light. Zinc-white is also prepared by exposing metallic zinc to the action of superheated steam, hydrogen being at the same time evolved, and used for illuminating purposes, as at Narbonne, St. Chinian, Céret, and a few other places, where it is known as platinum-gas, because the flame is used for imparting a white heat to small coils of platinum wire, thus producing a very steady and highly pleasant light. As regards the use of zinc-white as a pigment, it is rather more expensive than white-lead, yet according to some is a better covering material in the surface proportion of 10 to 13, that is to say, 13 parts by weight of zinc-white cover as much space as 10 of white-lead; moreover, zinc-white is not affected by sulphuretted hydrogen. Like white-leaf, this compound may be mixed with other pigments. By mixing Rinmann's green with it a green colour may be obtained; blue with ultramarine; lemon-yellow with cadmium orange-yellow (sulphuret of cadmium).

White Vitriol, Sulphate of Zinc. Zinc-vitriol ($SZnO_4 + 7H_2$), sulphate of zinc or white vitriol, is found as a native mineral, as a product of the oxidation of zinc-blende; it is also prepared by dissolving zinc in dilute sulphuric acid, and by roasting native zinc sulphuret. This vitriol occurs in white agglomerated crystals and in small acicular shaped crystals, as purified sulphate of zinc; it is used as a "dryer" in oil paints and varnishes; as a mordant in dyeing, for disinfecting purposes, and sometimes as a source of oxygen, since, on being submitted to a red heat, it gives off sulphurous acid and oxygen, oxide of zinc remaining.

Chromate of Zinc. This preparation, obtained by precipitating a solution of sulphate of zinc with bichromate of potassa, is a very fine yellow-coloured powder, used now and then in pigment printing, because it is soluble in ammonia, and thrown down again as a powder insoluble in water when that menstruum is volatilised. A basic chromate of zinc is used as a pigment in the paint trade.

Chloride of Zinc. This compound of zinc, $ZnCl_2$, is obtained either by dissolving zinc in hydrochloric acid, or more cheaply by causing the hydrochloric acid gas given off in manufacturing soda to act upon native sulphuret of zinc. By this action sulphuretted hydrogen is formed, which can be burned to produce sulphurous acid for the sulphuric acid chambers. The solution of chloride of zinc thus obtained is evaporated to the consistency of a syrup.

Anhydrous chloride of zinc is obtained by heating an intimate mixture of dried sulphate of zinc and chloride of sodium; chloride of zinc is formed which sublimes, and sulphate of soda which is left behind ($ZnSO_4 + 2NaCl = Na_2SO_4 + ZnCl_2$). This anhydrous chloride may be sometimes advantageously used instead of strong sulphuric acid, for instance in rape and colza oil refining, and perhaps, although it would be more expensive and less manageable, in the manufacture of garancine from madder. This chloride has of late been applied instead of sulphuric acid in the manufacture of stearic acid, and in the preparations of ether and parchment paper. Chloride of zinc in a strong and crude solution is largely and very successfully used for preserving timber; in paper-making for the decomposition of bleaching powder for bleaching the half-stuff and rags, and also in sizing the paper. The disinfectants sold as Sir William Burnett's Fluid and Drew's Disinfectant are solutions of chloride of zinc. The salt used in soldering iron, zinc, pewter, &c., is a compound of the chlorides of zinc and ammonium ($2NH_4Cl + ZnCl_2$); its solution is obtained by dissolving 3 parts by weight of zinc in strong hydrochloric acid, and adding, after the solution is complete, an equal weight of sal-ammoniac. Oxychloride of zinc, obtained by mixing oxide of zinc with a concentrated solution of chloride of zinc, or with solutions of chlorides of iron or manganese, has been recently proposed by M. Sorel as a plastic mass suited for stopping hollow teeth.

CADMIUM.

($Cd = 112$; Sp. gr. $= 8\cdot6$.)

This metal is rather rare, and as yet of very limited use; it is a constant companion of zinc in varying quantities, but is only found in the Silesian zinc ores in sufficiency to repay the trouble of extraction. It was discovered as a distinct metal by Dr. Stromeyer, at Hanover, and Dr. Herman, at Schönebeck, in 1817. As regards its properties, cadmium stands between zinc and tin; the colour and metallic lustre of cadmium are similar to those of tin; it is ductile and malleable, but more readily acted upon by atmospheric oxygen and moisture than tin. The specific gravity of cadmium is 8·6; it melts when quite pure in an atmosphere of dry hydrogen at 320°, and boils and volatilises (air and oxygen being absent) at 860° to 746·2°. The cadmium sold by manufacturing and operative chemists and opticians is in small round bars, weighing from 60 to 90 grms. Silesian calamine ore contains about 5 per cent. cadmium; the same ore found near Wieslock 2 per cent.; the zinc-blende found at the Upper Harz contains from 0·35 to 0·79 per cent. cadmium; zinc-blende from Przibram, Hungary, 1·78 per cent.; and the zinc ore of Eaton, in North America, about 3·2 per cent. cadmium. Such ores give off, while being heated in the zinc furnace, a brownish-coloured smoke, consisting of carbonate of zinc and metallic cadmium; this smoke, condensed separately, is used as cadmium ore, and reduced by means of charcoal, the materials being placed in iron retorts and the metal distilled over, next refined, and cast in the small bars mentioned above. The annual production of cadmium in Belgium from Spanish zinc ores amounts to about 5 cwts.; while Silesia produces some 2 cwts. annually.

Mixed with lead, tin, and bismuth, cadmium forms the so-called Wood's alloy or fusible metal, consisting of cadmium, 3 parts; tin, 4; bismuth 15; and lead 8 parts; this alloy fuses at 70°, and is used for stopping teeth, and for soldering surgical instruments. M. Hofer-Grosjean used as stereotype metal an alloy consisting of lead 50, tin 36, and cadmium, 22·5 parts. The only preparation of cadmium technically used to any extent is the cadmium-yellow, *jaune brilliant* (CdS), sulphuret of cadmium, applied as a pigment in oil painting, and in pyrotechny for producing blue-coloured flames. This preparation is best obtained by precipitating a solution of sulphate of cadmium with sulphuret of sodium, and then thoroughly washing, pressing, and drying the precipitate. Dr. Van Riemsdijk, of the Utrecht Mint, while experimenting with cadmium and zinc, both pure and kept fused in an atmosphere of pure dry hydrogen, found that these metals, though perfectly non-volatile at their point of fusion, and while kept fluid at that temperature, became perceptibly volatilised at a few degrees above this point.

ANTIMONY.

($Sb = 122$; Sp. gr. $= 6\cdot712$.)

Antimony. This metal, also named stibium, is chiefly found in combination with sulphur as black antimonial ore, or glass of antimony, containing 71·5 per cent., of metallic antimony, formula (Sb_2S_3), in veins interspersed among granite and metamorphic rocks. Antimony also occurs as oxide (Sb_2O_3) in the minerals known as Valentinite (rhombic) and Senarmontite (tesseral), this last variety being found in large quantities in Constantine, Algeria, and in Borneo. The black sulphuret of antimony is separated from the gangue which contains it by the application of heat, as the sulphuret is very fusible.

The operation is carried on at Wolfsberg, near Harzgerode, Germany, by placing the broken-up ore and gangue in crucibles, *b* (Fig. 42), perforated at the bottom, and placed on a smaller crucible, *c*, surrounded with hot sand or ash. The walls are of brickwork, so constructed with openings for causing a draught as to convey most heat to the upper crucible. Wood is used as fuel. In other localities, especially in Hungary, the apparatus exhibited in section and plan in Figs. 43 and 44 is used. As will be seen the principle is the same, but both the crucibles containing the ore, and the receiving crucibles outside the furnace, and connected by means of tubes with the inside crucibles, are more conveniently placed. The liquation of the rather fusible antimony ore is most readily and conveniently performed in the hearth of a peculiarly constructed reverberatory furnace, exhibited in Fig. 45; the main point of the arrangement of the hearth being that the molten black sulphuret, collected at the lowest level, runs through the spout, *c*, to the receiver, *f*, placed outside the furnace. At first a moderate heat suffices, but towards the latter part of the operation a strong heat is required to eliminate all the sulphuret. The opening at *f* is now closed with a plug. Not until the gangue becomes semi-fused is the operation finished, when the heavier sulphuret collected under the slag is run off by the opening of the plug at *f*.

FIG. 42.

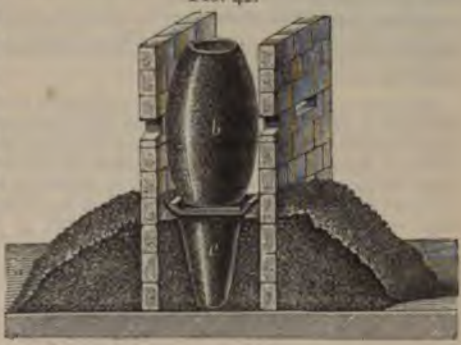


FIG. 43.

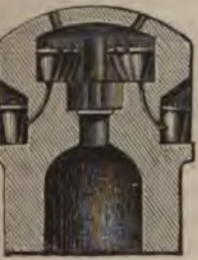


FIG. 44.

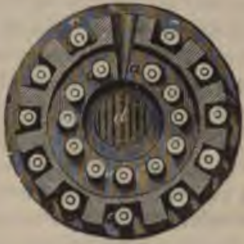
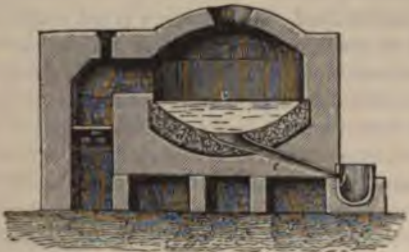


FIG 45.



Metallic antimony is obtained from the black sulphuret, either by roasting or by smelting it with suitable fluxes. In the former instance the sulphuret is placed on the hearth of a reverberatory furnace and continuously stirred, while a supply of air has access to the molten mass; the calcination is continued until the bulk of the ore is converted into antimoniate of antimony-oxide. This material, also known as antimonial ash, is reduced to metal in crucibles, and for the reduction heat alone would answer, as the calcined ore always contains undecomposed sulphuret of antimony ($3Sb_4O_8+4Sb_2S_3=20Sb+12SO_2$); but as some oxide of antimony would be lost by volatilisation, the crude antimonial ash is mixed with crude argol or with charcoal-powder and carbonate of soda. A strong red heat is sufficient for the reduction, and it is customary to allow the metal to cool slowly under the supernatant slag, in order to obtain the peculiar crystalline appearance desired in metallic antimony in the trade.

By another mode of operation the sulphur is first removed from the black sulphuret by means of iron, but which, if used by itself, presents a difficulty arising from the almost equal specific gravities of the metallic antimony and sulphuret of iron, rendering the separation of these substances too imperfect to admit of the use of iron alone; consequently, either carbonate or sulphate of soda or potassa is added, which tends also to increase the fluidity of the slag. 100 parts of black sulphuret of antimony, 42 parts of malleable iron, 10 parts of dry sulphate of soda, and 3½ parts of charcoal powder are the proportions. In order to eliminate the arsenic from the metallic antimony thus obtained, 16 parts are taken, and there are added 2 parts of protosulphuret of iron, 1 of sulphuret of antimony, and 2 of dry soda; this mixture is kept fused for fully one hour's time, the resulting metal is next fused with 1½ parts of soda, and a third time with 1 part of soda, until the supernatant slag attains a bright yellow colour.

Properties of Antimony. The metallic antimony of commerce is never quite free from arsenic, iron, copper, and sulphur; the influence of these impurities on the physical properties of antimony is not well ascertained, as those of chemically pure antimony are not well known.

Antimony may be purified by fusing it with oxide of antimony; the sulphur and iron are oxidized and some of the oxide of antimony reduced to metal. For pharmaceutical purposes antimony is purified by the addition to the molten metal of pure saltpetre, but this process is attended with a loss of antimony. Antimony possesses a nearly silver-white but slightly yellowish colour, strong metallic lustre, and a foliated crystalline structure; it crystallises like arsenic and bismuth in rhomboidic crystals. The specific gravity of antimony is $=6{\cdot}712$; it melts at 430°, the pure metal fuses at 450°, and, according to Dr. Duflos, does not expand on cooling. Antimony is volatilised, air and oxygen being excluded, only at a bright white heat. It is a very brittle metal, neither ductile nor malleable, but harder than copper. Antimony forms alloys readily, imparting to them some of its own brittleness and hardness; it is, therefore, added to tin, lead, and pewter, in small quantities, to render these soft metals hard. As antimony is not readily acted upon by air, it has been suggested to electrotype copper with a thin layer of this metal. The powder sold as ironblack, and used to give to *papier maché* and plaster of Paris figures the appearance of polished steel, is finely divided antimony, obtained by precipitating that metal from its solution in an acid by means of metallic zinc; this powder is also used to impart a lustre to cast zinc ornaments. The chief use made of antimony is as an alloy for printing type, which usually consists of 4 parts of lead and 1 of antimony with a small quantity of copper. Antimony also enters into the hard so-called anti-friction alloys used for the bearings of machinery.

ANTIMONIAL PREPARATIONS IN TECHNICAL USE.

Oxide of Antimony. This substance (Sb_2O_3), obtained by calcining sulphuret of antimony, or by the precipitation of a solution of chloride of antimony with a solution of carbonate of soda, finally washing and drying the precipitate, has of late been used as a substitute for white-lead, but does not cover so well and is more expensive, though it is not affected by sulphuretted hydrogen. As this oxide takes up oxygen in the presence of alkalies, and is converted into antimonic acid (Sb_2O_5), it has been lately proposed for use in the preparation of aniline red and for the conversion of nitrobenzol into aniline; also for the preparation of iodide of calcium by keeping antimonic oxide suspended in milk of lime, and adding iodine as long as the latter is taken up.

Black Sulphuret of Antimony. This compound (Sb_2S_3), obtained by liquation, occurs in commerce in the conical shape it has assumed while cooling; its colour is like that of graphite, but it has a stronger metallic lustre, is of a deeper black colour, fibrous, crystalline structure, and very brittle; it usually contains iron, lead, copper, and arsenic, and is employed for separating gold from silver, in veterinary surgery, pyrotechny, and in the preparation of the percussion pellets used in the cartridges of the now celebrated Prussian needle-gun.

Neapolitan Yellow. This pigment, used as an oil paint and in glass and porcelain staining, is of an orange-yellow colour, and very permanent. It is antimoniate of oxide of lead, and is prepared as follows:—1 part of antimonio-tartrate of potassa (tartar emetic), 2 parts of nitrate of lead, and 4 parts of common salt, are fused at a moderate red heat, and kept at that temperature for 2 hours. The molten mass is put after cooling into water and becomes disintegrated, the salt dissolved and the pigment precipitated. When required for staining glass or porcelain it is mixed with a lead-glass, and has recently been prepared by roasting a mixture of antimonious acid and litharge.

Antimony Cinnabar. Oxysulphuret of antimony ($Sb_6S_6O_3$), is a compound in colour similar to vermillion, and is obtained by causing dithionite of sodium or calcium to act upon protochloride of antimony in water, and boiling this mixture, a precipitate being readily deposited; it is a soft, velvety powder, unaltered by the action of air and light, and suited for either oil- or water-colour. This substance may be prepared on a large scale by the following process:—(1.) Black sulphuret of antimony is calcined in a current of air and steam, antimonic oxide being formed as well as sulphurous acid, which may be employed for the preparation of calcium-dithionite from soda waste; the antimonic oxide is next dissolved in crude hydrochloric acid. (2.) Large wooden tubs which admit of being internally heated by steam, are for ⅞ths of their capacity filled with the solution of calcium dithionite, and the solution of protochloride of antimony is gradually added, the liquid being stirred and heated to about 60°; the reaction soon ensues, and the precipitate having subsided, is thoroughly washed and dried at a temperature not exceeding 50°. There are prepared on a large scale, by operative pharmaceutical and manufacturing chemists, numerous varieties of antimonial preparations, among which are several sulphurets and one oxysulphuret, different from the preparation here mentioned.

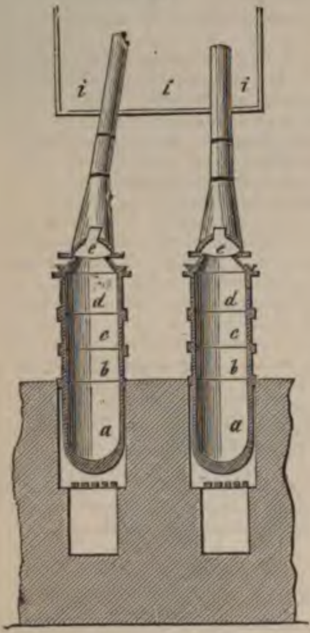
ARSENIC.

($As = 75$; Sp. gr. $= 5{\cdot}6$.)

Arsenic. Arsenic occurs in the mineral kingdom either native or in combination with sulphur. Although a few minerals are found containing arsenic in a state of oxidation, the quantity is so small that their technical utilization for the obtaining of arsenical compounds is altogether out of the question. Metallic arsenic is a solid, cystalline, steel-grey coloured substance. It is prepared either by the sublimation of the native metal, or by the ignition of arsenical iron pyrites ($FeS_2 + FeAs_2$) and of arsenical pyrites (Fe_4As_6), or by the reduction of arsenious acid ($As_2O_3 + 3C = 3CO + As_2$). Metallic arsenic is met with in the trade in an impure state, often containing no less than 10 per cent. of sulphuret of arsenic, in the form of greyish-black coloured crusts and lumps, known as fly poison. Pure metallic arsenic is rarely employed; a small quantity is used in the manufacture of shot, and in pyrotechny for white Bengal fire, which gives a very brilliant light, but should only be ignited in the open air. Lastly, arsenic burnt in oxygen gas is used as signal lights in the Trignometrical Survey Service.

Arsenious Acid. The substance known as white arsenic is really arsenious acid, As_2O_3, and obtained as a by-product of a great many metallurgical operations, for instance, the roasting of cobalt ores for smalt, of tin and silver ores; the volatilised acid is condensed by conducting it through channels into wooden chambers. In some localities, as in Silesia, where fuel and labour are cheap, arsenical pyrites is purposely calcined, and the crude arsenious acid obtained is refined by another sublimation process. For this purpose the cast-iron vessels, *a*, Fig. 46, are used, upon which are placed iron rings or collars, *b*, *c*, *d*, and a hood *e*, communicating by means of tubes with a series of chambers, of which the first only is shown in *i*. The flanges of the cast-iron collars and all other joints having been thoroughly luted, the fire is lighted and the heat so increased as to cause the semi-fusion of the arsenious acid, which after cooling exhibits a peculiarly porcelain-like appearance, at first being as transparent as glass and very similar to fused anhydrous phosphoric acid.

Fig. 46.



This compound, like *all* arsenical preparations is very poisonous; but it is a remarkable fact, proved by direct experiment, that pure metallic arsenic introduced into the stomach of rabbits and other small animals in a finely divided state, by the aid of pure water freed from air, does not act on them as a poison, being found in their fæces unaltered. The commercial article is sometimes more or less mixed with oxide of antimony and sulphuret of arsenic. Arsenious acid is used in dyeing and calico-printing, in glass-making, for the purpose of clearing the molten glass, for the preparation of other arsenical compounds and pigments, and further in arsenical soap for the preservation of stuffed animals. The air in museums is sometimes poisoned by arseniuretted hydrogen being evolved if the arsenical compound has not been properly prepared; and in places where there are large collections of stuffed animals there should always be a good ventilation and a dry atmosphere. Arsenious acid is also employed in the manufacture of aniline.

Arsenic Acid. This acid (H_3AsO_4) has become an article of large consumption. it is obtained by boiling 400 kilos. of arsenious acid in 300 kilos. of nitric or nitrohydrochloric acid, and evaporating the solution to dryness. Recently it has been prepared more cheaply by passing chlorine gas into water wherein arsenious acid is suspended, and evaporating this solution. Arsenic acid is sometimes employed in calico-printing instead of tartaric-acid, and is very largely used in the preparation of rosaniline or fuchsine, some manufacturers of these dyes annually consuming 2000 cwts.

The acid arseniate of soda, so-called dungsalt, now used instead of cows'-dung in certain calico-printing operations, and consisting of 25 parts of soda and 75 ot arsenious acid, is prepared by heating for a length of time, either 36 parts of arsenious acid, and 30 parts of nitrate of soda, or a mixture of arsenite of soda and nitrate of soda. This salt is obtained as a by-product of the preparation of aniline from nitrobenzol.

Sulphurets of Arsenic. There are two sulphurets of arsenic employed industrially, viz., realgar and orpiment.

Realgar. Red arsenic or realgar (As_2S_2) is found native in a crystalline state and among other ores. It is artificially prepared by fusing together sulphur and excess of either metallic arsenic or arsenious acid, or on a large scale by distilling arsenical pyrites and ores containing sulphur. Realgar is a ruby-red coloured substance, exhibiting a conchoidal fracture. Its use in pyrotechny is based upon its property of yielding, when mixed with saltpetre and ignited, a brilliant white light. This mixture is known as Bengal white light, and is best prepared with 24 parts of nitrate of potassa, 7 parts of sulphur, and 2 parts of realgar.

Orpiment. *Auri pigmentum*, yellow sulphuret of arsenic (As_2S_3), is likewise found native, but is generally artificially prepared by fusing together either sulphur and arsenious acid or realgar and arsenious acid. This sulphuret is of a bright orange-colour, somewhat transparent; it contains, if prepared by the dry method, free arsenious acid, and may therefore be considered as arsenoxysulphuret. It is also prepared by precipitating a hydrochloric acid solution of arsenious acid by means of sulphuretted hydrogen, or by decomposing a solution of the double sulphuret of arsenic and sulphuret of sodium with dilute sulphuric acid. **Rusma.** Orpiment is used in dyeing to reduce indigo, and to prepare what is termed rusma, a paste applied in dressing skins in order to remove the hair, and which consists of 9 parts of lime and 1 of orpiment mixed with water. This paste is also employed in the toilet to remove superfluous hair; but instead of this very poisonous compound, either the spent lime from the purifiers of gasworks, or the sulphuret of lime solution obtained by passing a current of sulphuretted hydrogen through milk of lime, may be advantageously used.

QUICKSILVER, OR MERCURY.

($Hg = 200$; Sp. gr. $= 13{\cdot}5$.)

Occurrence and Mode of Obtaining Mercury This metal is not met with so generally dispersed as silver and gold. It occurs in the following forms:—1. Sparingly in the metallic state interspersed in globules through the gangue, and in small quantities in mercury mines, sometimes containing silver. 2. As a sulphuret, known as cinnabar, HgS, containing 86·29 of metallic mercury and 13·71 of sulphur. This ore is met with among primitive as well as metamorphic and sedimentary rocks, and is often accompanied by sulphuret of iron, while the gangue or matrix is generally quartz, calcareous spar, or spathic iron ore. The richest mercury mines are those of Almaden and Almadenejas in Spain, which were worked at a remote period of antiquity, and next are those of Idria, Carynthia. Cinnabar is found also in the Rhenish Palatinate, at Olpe in Westphalia, Horzowitz in Bohemia, in various parts of Hungary, at Vall'alta in Venetia, in the Oural, in China and Japan, in Borneo, Mexico, at Huancavelica, in Peru, and in considerable quantities in California, where mercury is largely produced.

Among the less important mercury ores is found the so-called liver-coloured ore, a clay mixed with cinnabar, bitumen, paraffine, and coal-slate. This ore is only met with in Carynthia. There is also the fawn-coloured mercury ore, containing 2 to 15 per cent. of mercury, with sulphur, copper, and other impurities. The annual production of mercury throughout the globe amounted in 1870, to 84,500 cwts., of which California yields 56,000 against 22,000 from Spain.

Mercury is extracted from its chief ore, cinnabar, by:—

1. Calcination in shaft furnaces, the mercurial vapours being condensed in chambers constructed either of brickwork or boiler-plate, or in earthenware vessels (Aludels) joined together by flanges similar to earthenware drain-pipes.
2. By decomposing cinnabar in closed vessels, the ore being mixed with either lime or forge scales. This method is usual in Bohemia and the Bavarian Palatinate.

Method of Extracting Mercury pursued in Idria. The contrivances in use in Idria for the extraction of mercury from its ores are illustrated in Figures 47, 48, and 49. A is a calciantion furnace, which is flanked on each side by a series of condensation chambers, C C D, communicating with the furnace. The ore is placed in lumps on the perforated arches, *n n′*, of the furnace, and the space V completely filled. On the arch, *p p′*, the smaller lumps of ore are placed, and on *r r*, the dust, pulverulent ore, and residues of former operations. This having been done, the fuel, commonly dry beechwood, is ignited on the furnace-bars. The heat is gradually raised to and kept at a dark red heat for 10 to 12 hours. The draught created carries into the furnace sufficient air to convert the sulphur of the volatilised ore into sulphurous acid and set the mercury free ($HgS + {}_2O = SO_2 + Hg$). The products of the combustion are carried into the chambers, C. The bottom of each chamber is made of strongly pressed clay, shaped so as to form two planes inclined towards each other, and connected with gutters leading to a reservoir cut out of a solid block of porphyry in which the mercury is collected. A jet of water is made to play constantly in the last condensation-chamber, in order to keep it and the adjoining smoke-chambers, D D, quite cool, the last traces of mercury being condensed in D D.

FIG. 47.

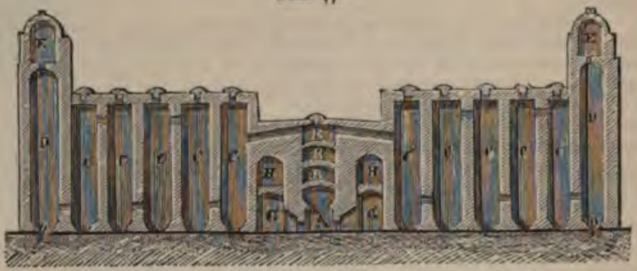


FIG. 48.

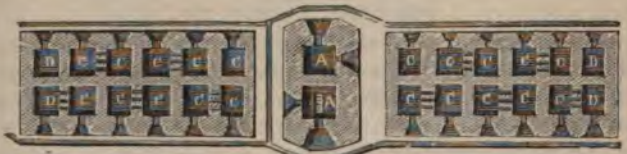
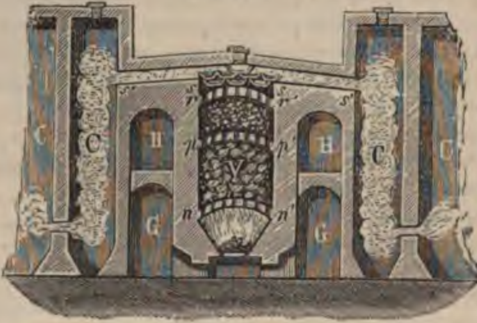


FIG. 49.



Very recently experiments have been made at Idria to distil he mercury continuously from its ore by the use of a reverberatory furnace, whereby both time and fuel are saved.

Spanish Method of Extracting Mercury. The arrangement for condensing the mercurial vapours in use at Almaden is exhibited in Fig. 50. It consists of a string of pearl-shaped vessels open at both ends. These vessels, locally known by the Arabian term, *Aludels*, are made of earthenware, and so constructed that the narrow end of one fits into the wider end of the other, care being taken to lute the joints with clay. The mode of arranging these rows or strings of aludels is delineated in Fig. 52, which represents the plan of the furnace shown in Fig. 51. This furnace consists of a cylindrical shaft oven, which by means of a perforated arch is divided into two parts. The fire is lighted in the lower part of the shaft, while on the perforated arch is first placed a layer of sandstone containing cinnabar, in quantities too small to admit of being otherwise advantageously treated. The rich ore is then placed on this layer of stone, and the openings in the arch of the furnace covered with tiles and tightly luted. The mercurial vapours are first conducted into the space *c c*, and thence through the twelve rows of aludels, each row having a length of from 20 to 22 metres, and containing 44 aludels. The aludels are placed on a somewhat inclined plane as shown in the woodcut. At *f* the condensed mercury is run off by

FIG. 50.

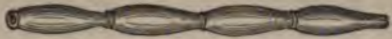


FIG. 51.

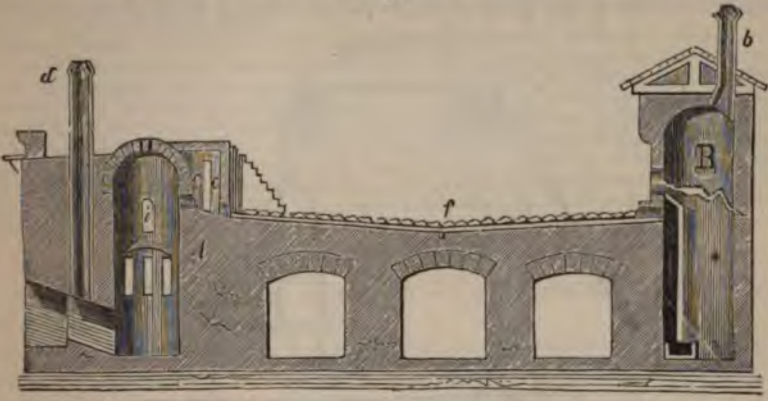
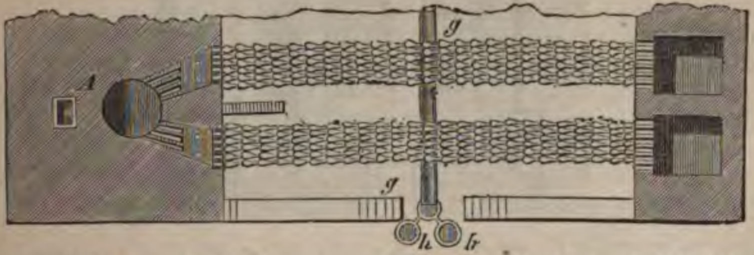


FIG. 52.

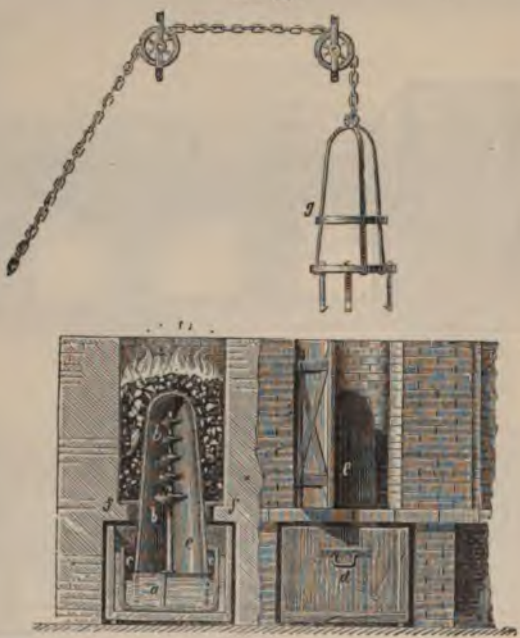


the gutter, *g*, into the stone cisterns, *h h*; the vapours not condensed being carried on to the chamber, B, where they are completely liquefied. The smoke escapes through a chimney at *b*. As the mercury thus obtained is mixed with soot it has to be purified and cleansed; this is effected by causing the metal to flow down an inclined plane, to which the soot adheres. The sooty mass and the impurities collected in the room B, are submitted to distillation for the purpose of extracting the last traces of mercury. The quantity of ore operated upon at each calcination amounts to 250 to 300 cwts. Spanish mercury is met with in the trade packed in wrought-iron canisters or in sheepskin bags. The apparatus above described for separating mercury from its ores was invented by the Moors, who for several centuries were the only civilised inhabitants of the greater portion of southern Spain.

Method of Decomposing the Ore by the aid of other Substances.

Method of mercury distillation pursued at Horzowitz in Bohemia. The sulphuret of mercury is mixed with from $\frac{1}{4}$ to $\frac{1}{3}$ of its weight of forge-scale, and the mixture placed on the iron plates, *b b*, Fig. 53. These plates are fixed to an iron rod, and covered by the iron cupola, *e e*, which rests in a tank filled with water. The cupola is removable from the furnace by means of the frame *g*. The metal is collected in the water at *d*. Each cupola covers about $\frac{1}{2}$ cwt. of ore and $\frac{1}{4}$ cwt. of forge-scale, and there are generally six cupolas in one furnace. The operation lasts for 30 to 36 hours.

FIG. 53.



In the Rhenish Palatinate mercury has been extracted from its ores since 1410. It is there usual to mix the mercury ore with other metallic ores, that mainly worked being cinnabar interspersed in sandstone. The decomposition of the ore, which is a rather poor material, can be made to pay only by skilful management. The ore is mixed with lime and placed in iron retorts, very similar to those used in gas-works, and heat having been applied the cinnabar is decomposed, the result being the formation of metallic mercury, which volatilises and is condensed in suitably-constructed receivers, while there remains in the retorts a mixture of sulphuret of calcium and hyposulphite of lime. The operation lasts ten hours, after which the contents of the receivers are poured into earthenware tanks filled with water; the mercury sinks to the bottom and the water is allowed to run off, carrying with it a blackish powder, consisting of finely-divided mercury mixed with a volatilised black sulphide, which is again submitted with lime to another distillation.

Properties of Mercury. Mercury is the only metal remaining fluid at ordinary temperatures. It freezes at $-32\cdot5°$, and is in that state a malleable and ductile metal. At 360° it boils, and at a slightly higher temperature distils over, but is volatilised to some extent at all temperatures above its freezing-point, as may be proved by suspending a piece of gold-leaf in the neck of a bottle containing a small quantity of mercury. Mercury readily combines at ordinary temperatures with various metals, forming what are termed amalgams. The amalgams most readily formed are those of lead, bismuth, zinc, tin, silver, gold; next is that with copper, while with iron, nickel, cobalt, and platinum, mercury will only amalgamate with difficulty. The application of mercury in metallurgy in the extraction of gold and silver from their ores is based upon the property mercury possesses of readily combining with these metals. Amalgams of various kinds are industrially employed, as, for instance, with tin for covering mirrors and looking-glasses, with gold for the so-called process of fire-gilding. An amalgam of 4 parts mercury with 2 parts zinc and 1 part tin is used for the cushions of electrical machines.

Applications of Mercury. By far the most extensive application of mercury is in the construction of various physical instruments, for filling the mercurial gauges of steam-boilers, and on the Continent these gauges are attached to all boilers, locomotive engine-boilers alone excepted. Mercury is employed in the preparation of a variety of compounds, among which is the fulminate of mercury; and, further, for various purposes in chemical and physical laboratories. More recently, an amalgam of mercury and sodium has been very successfully used by Mr. Crookes in the metallurgical extraction of silver and gold; and a solidified amalgam of the same metals is recommended to facilitate the transport of mercury, the amalgam admitting of being very readily decomposed by treating with dilute sulphuric acid.

PREPARATIONS OF MERCURY.

Mercurial Compounds. The more important mercurial compounds which are manufactured on the large scale are the following:—

Mercuric Chloride. The substance commonly known as corrosive-sublimate is the perchloride of mercury, $HgCl$, equivalent$=135$, consisting, in 100 parts, of 73·8 parts of mercury and 26·2 parts of chlorine. It is prepared either by sublimation from a mixture of sulphate of peroxide (red oxide) of mercury and common salt, or by dissolving the same oxide in hydrochloric acid, and also by boiling a solution of chloride of magnesium with the peroxide ($MgCl_2+HgO=HCl+MGO$). When sublimed, this salt forms a white crystalline mass, which fuses at 260°, boils at 290°, is soluble in 13·5 parts of water at 20°, and in 1·85 parts of the same liquid at 100°. It is more readily dissolved by alcohol, 1 part of the salt requiring only 2·3 parts of cold and 1·18 parts of boiling alcohol. Mercuric-chloride has been industrially employed as a preservative for timber by Mr. Kyan, and is used in the manufacture of aniline-red, in dyeing, and calico-printing, in etching on steel-plates, and for the preparation of other mercurial salts. Lately, the use of the double salt, $HgCl_2,2KCl$, obtained by boiling chloride of potassium with peroxide of mercury, has been suggested as a preservative for timber. It should be borne in mind that this preparation of mercury is extremely poisonous, and easily absorbed by the skin of the hands.

Cinnabar. Under this name is designated the mercuric-sulphide, HgS, which occurs native in crystalline or compact red-coloured masses, and was known in Pliny's time by the term minium.* The cinnabar, or vermillion of commerce, used as a pigment, is always artificially prepared either by the dry or wet way. By the former process 540 parts of mercury and 75 of sulphur are very intimately mixed. The ensuing black-coloured powder is introduced into iron vessels, and exposed to a moderate heat so as to cause the fusion of the mass, which, after cooling, is broken up and then introduced into earthenware and loosely closed vessels, heated on a sand-bath. The sublimed mass is of a cochineal-red colour, exhibits a fibrous fracture, and yields when pulverised a scarlet powder, which is the more beautiful the purer the materials used in its preparation and the greater the care taken to avoid an excess of sulphur. Some chemists-allege that a greatly improved vermillion is obtained if 1 part of sulphuret of antimony is added to the mixture of sulphur and mercury previously to the sublimation, and the sublimed and pulverised mass placed in a dark room for several months and treated with either dilute nitric acid or caustic potassa. According to Dr. J. von Liebig, vermillion is obtained in the wet process by treating the white precipitate of the Pharmacopœia, or *hydrargyrum amidato bichloratum*, according to the formula, $HgCl,HgNH_2$, which corresponds to the term used, but in Dr. A. W. Hofmann's opinion, does not express the true composition of the compound. He considers white precipitate to be a chloride of ammonium, in the ammonium of which 2 equivalents of mercury have taken the place of 2 equivalents of hydrogen; formula $N\left\{\begin{matrix}H_2\\Hg_2\end{matrix}\right.$. Other chemists, again, hold different views as to the constitution of this body, which has been used in medicine since, if not before, the time of Paracelsus. Vermillion is generally obtained by precipitating a solution of corrosive-sublimate in ammonia with a solution of sulphur in sulphide of ammonium; or, according to Dr. von Martius, by agitating, in a suitable vessel, 1 part of sulphur, 7 of mercury, and 2 to 3 of a concentrated solution of liver of sulphur. According to M. Brunner's method, by which decidedly the finest vermillion is obtained, 114 parts by weight of sulphur and 300 parts by weight of mercury are mixed, with the addition of a small quantity of caustic potassa solution, and incorporated by being shaken by machinery. The resulting black compound is next treated with a solution of 75 parts caustic potassa in 400 parts of water, and heated on a water-bath to 45°. The mixture assumes a scarlet colour after a few hours, and as soon as this is apparent the semi-liquid mass is poured into cold water, next collected on filters, washed, and dried. The vermillion of commerce is often adulterated with red-lead, peroxide of iron, chrome-lead, and more frequently with from 15 to 20 per cent. of gypsum. These adulterations are, however, readily detected, as they are left behind when the vermillion is sublimed. Red-lead, one of the most usual adulterations of vermillion, can be readily detected either by treating a small quantity of the suspected sample with nitric acid, when in consequence of the formation of puce-coloured peroxide of lead, the mass assumes a brown colour, or by the addition of hydrochloric acid, when chlorine is given off. Pure cinnabar is completely and readily soluble in hydrosulphuret of sulphide of sodium ($NaSH$).

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* Red-lead, afterwards called minium, was, as far as it appears, unknown to the ancients, being first prepared by the Arabs and Saracens.

Fulminating Mercury. The compound known as fulminating mercury is a combination of fulminic acid, an acid unknown in a free state, and of oxide of mercury; its formula may be written $C_2Hg_2N_2O_2$. In 100 parts it consists of 77·06 of peroxide of mercury and 23·94 of fulminic acid. According to the late Dr. Gerhardt's view, this body is a nitro-compound which may be regarded as cyan-methyl, the hydrogen of the methyl of which has been replaced by hyponitric acid and mercury; the formula is then: $C\left\{\begin{matrix}Hg_2\\NO_2\end{matrix}\right\},CN$. This substance was first discovered by Mr. Howard, and was known, until Dr. von Liebig gave the clue to its nature, as Howard's detonating powder. It is prepared on a large scale in the following manner. First, 2 lbs. of mercury are dissolved, by the aid of a gentle heat, in 10 lbs. of nitric acid (sp. gr. 1·33), and 10 lbs. more of nitric acid are then added. The resulting fluid is poured into six tubulated retorts, and to the contents of each retort is added 10 litres of alcohol (sp. gr. 0·833). If the ingredients are mixed by measure instead of weight, for every volume of mercury, there is taken 7½ volumes of nitric acid, and 10 volumes of alcohol. After a few minutes a strong evolution of gas takes place, and at the same time a white precipitate, the fulminate of mercury, is formed. The retorts are fitted with tubulated receivers, from which glass tubes carry off the very poisonous gas and fumes, either to a flue or directly to the outside of the shed in which the operation is performed. The precipitate is collected on filters, and washed with cold water to eliminate the free acid. The fulminate is next dried, filtered, and all being placed on plates of copper or earthenware, heated by steam to less than 100°. 100 parts of mercury yield in practice from 118 to 128 parts of fulminate, while, according to theory, 142 should be obtained. The dried fulminate is, with cautious manipulation, divided into small portions, kept separately in a paper bag. The fulminate thus prepared is a crystalline white-coloured substance, which, by being heated to 186°, or by a smart blow, explodes with a loud report. When placed on iron and struck with an iron instrument, the detonation is much increased. This substance also explodes by contact with concentrated sulphuric acid. When mixed with 30 per cent. of its weight of water, the crystalline fulminate may be rubbed to powder with a wooden pestle on a marble slab. The manufacture of this substance on a large scale requires peculiar arrangements, into the particulars of which we cannot here enter.

Percussion-Caps. The fulminate of mercury is chiefly used for filling percussion-caps. For this purpose 100 parts of the fulminate are rubbed to powder with 30 parts of water, 50 to 62·5 parts of saltpetre, and 29 of sulphur. This mixture is dried sufficiently to admit of being granulated, after which it is forced, by means of machinery, into the copper caps, and simultaneously covered with either a layer of varnish or tin-foil, to protect it from damp. Tin-foil being more expensive is not used for military gun-caps. The best varnish for the purpose is a solution of mastic in oil of turpentine. The caps are finally dried by a gentle heat, and packed in boxes. One kilogramme of mercury converted into fulminate suffices for the filling of 40,000 gun-caps of the larger or military size, and for 57,600 caps of the size used by sportsmen.

PLATINUM.

(Pt = 197·4; sp. gr. = 21·0 to 23·0.)

Occurrence of Platinum. This metal is only found native, and then not very abundantly, in platinum ore, more especially met with in the alluvial deposits of South America and the Oural, in grains of a steel-grey colour and metallic lustre. More recently, granules of metallic platinum have been found among the gold-washings in California, the Brazils, Haiti, Australia, and Borneo. A very short time ago this metal was discovered in Europe, interspersed in rocks situated in the parish of Roeraas, in Norway, and it is reported to have been found in the lead-mines near Ibbinbüren, in Westphalia. Dr. Pettenkofer states that a proof of the far greater dispersion of platinum than is generally supposed lies in the fact that all silver contains a small quantity of platinum. The metal has also been found to accompany some of the copper and antimony ores of Timor and New Guinea. Platinum was discovered in South America by the Spaniards, who, believing it to be an inferior silver, gave it the diminutive *platina* of the Spanish name for silver, *plata*. It was brought from Jamaica and made known in Europe by a Mr. Wood in 1740, and somewhat investigated in 1767 by Dr. R. Watson, then Professor of Chemistry at Cambridge Dr. Scheffer, Director of the Mint at Stockholm, was the first who thoroughly investigated the various physical and chemical properties of this metal in 1752; but as his researches were published in the Swedish language, they remained comparatively unknown in this country.

Platinum Ores. The substance met with in commerce under the name of platinum ore, or crude platinum, is a mixture of a variety of metals, among which the following predominate:—Platinum, palladium, rhodium, iridium, osmium, ruthenium, iron, copper, lead, and frequently granules of osm-iridium, gold, chrome-iron ore, titanium-iron ore, spinel, zircon, and quartz. The reason why this ore is found in alluvial soil is, that the rocks originally containing the ore having been disintegrated by water, it is carried off by the streams and water-courses. Boussingault found, when travelling in South America, a seam of somewhat weathered syenite containing the platinum ore yet *in situ;* while, as regards the Oural, it has been proved by Pallas that the ore was originally imbedded in serpentine-rock which has been washed away by water, the water, however, leaving such minerals as chrome-iron ore, zircon, titanium-iron ore, &c. In the Island of Borneo, platinum ore is mixed with sesqui-sulphuret of ruthenium, a mineral which has been named by Dr. Wöhler (1866) *Laurite.*

The composition of some platinum ores is exhibited in the following table:—Analysed by Dr. Berzelius, *a*, ore from the Oural; Dr. Svanberg, *b* and *c*, from Columbia and Choco; Dr. Bleekrode, *d*, from Borneo; Dr. Weil, *e*, from California.

	a.	*b.*	*c.*	*d.*	*e.*
Platinum	86·50	84·30	86·16	71·87	57·75
Rhodium	1·15	3·46	2·16	—	2·45
Iridium	—	1·46	1·09	7·92	3·10
Palladium	1·10	1·06	0·35	1·28	0·25
Osmium	—	1·03	0·97	0·48	0·81
Osm-iridium	1·14	—	1·91	8·43	27·65
Copper	0·45	0·74	0·40	0·43	0·20
Iron	8·32	5·31	8·03	8·40	7·70
Lime	—	0·12	—		
Quartz	—	0·60	—		

According to Dr. H. Deville, the average quantity of platinum contained in the following ores is:—

Columbia	76·80—86·20	per cent.
California	76·50—85·50	„
Oregon	50·45	„
Australia	59·80—61·40	„
Siberia	73·50—78·90	„
Borneo	57·75—70·21	„

The annual production of metallic platinum amounts to from 35 to 50 cwts., of which quantity the Oural yields 28 to 49 cwts., Columbia and the Brazils, 6 to 8 cwts.

Wollaston's Method of Extracting Platinum from its Ores.

The method originally devised by the late Dr. Wollaston, and still employed by the Parisian platinum-makers, Chapuis, Desmoutis, and Quennessen, is as follows:—The ore is first treated with cold aqua regia to dissolve any gold, and the liquid separated from the ore by filtration. The mineral is again treated with aqua regia in a retort, and heat applied; the distillate contains osmic acid, and the insoluble residue in the retort osm-iridium, ruthenium, chrome-iron ore, and titanium-iron ore. The acid liquid contains palladium, platinum, rhodium, and some iridium, in solution, and the acid having been neutralised with carbonate of soda, the fluid is mixed with cyanide of mercury, whereby palladium is separated as cyanide of palladium. That precipitate having been removed by filtration, the liquid, diluted with water, is next concentrated by evaporation, and then mixed with a concentrated solution of chloride of ammonium, the mixture resulting in a precipitate ($PtCl_4,2NH_4Cl$), of the double chloride of platinum and ammonium, containing only a trace of iridium, which, as it imparts greater hardness to platinum, is not injurious. The platinum sal-ammoniac, as the precipitate is industrially named, is first dried and afterwards ignited, leaving spongy platinum, which is forced by means of properly fitting pistons into steel tubes heated to redness, the operation being repeated as often as is required to obtain the metal in a compact coherent state. According to MM. Descotil and Hess, platinum ores should be first fused with from 2 to 4 times their weight of zinc, the cooled brittle mass pulverised, and treated with dilute sulphuric acid to eliminate some of the iron and zinc; the remaining substance is then treated with nitric acid, which dissolves the rest of the iron, copper, and lead. The ore is afterwards treated with aqua regia, which acts more readily on account of the fine state of division of the mineral. M. Jeannetty (Paris) found that platinum becomes readily fusible by the addition of metallic arsenic, which is afterwards volatilised.

Method of Deville and Debray. The excellent method introduced by MM. Deville and Debray, in 1859, is based upon the fact that metallic lead, while fusing with platinum ore, dissolves all the foreign metals, osm-iridium alone excepted. The platinum ore is consequently placed on the hearth of a reverberatory furnace, and having been mixed with its own weight of galena, a regulus is obtained, under which the osm-iridium is left, while a lead slag floats on the top, the iron decomposing a portion of the galena and producing metallic lead. The regulus is heated in a cupel furnace, whereby all foreign metals are volatilised or absorbed as oxides, leaving the metallic platinum, which is refined by being again melted in crucibles made of lime, which absorbs and eliminates all impurities, such as silicium, iron, copper, &c. The fuel used for this purpose is coal-gas, the combustion being kept up by means of oxygen. The smelting of 1 kilo. of platinum requires 100 litres of oxygen gas and 300 litres of coal-gas. The firm of Messrs. Johnson, Matthey, and Co., the most eminent and extensive platinum smiths in the world, exhibited at the International Exhibition of 1862 an ingot of pure platinum weighing no less than 2½ cwts., valued at £4,000, smelted by the method of MM. Deville and Debray. The molten platinum is afterwards submitted to the action of a steam-hammer to render it dense, solid, and fully malleable.

Properties of Platinum. This metal is nearly as white as silver, but with a steel-grey shade. It exhibits considerable lustre; is very malleable and ductile, and so soft that it readily admits of being cut with a pair of scissors. It may be drawn in wire thinner than a spider's web, an operation conducted by coating an already thin platinum wire with silver. The wire thus prepared is drawn out and the silver afterwards removed by nitric acid, which dissolves that metal but leaves the platinum. The specific gravity of platinum varies from 21·0 to 23·0. This metal admits of being welded at a white heat, and may be melted by the oxyhydrogen flame, its melting-point, according to Dr. Deville, being between 1460° to 1480°. Platinum occurs in commerce as spongy platinum, black platinum, forged or hammered and cast platinum.

Black Platinum. Spongy Platinum. Black and spongy platinum possess the property of absorbing and condensing large quantity of gases, more especially oxygen. If a jet of hydrogen is directed upon the spongy metal, black platinum being only an exceedingly finely divided spongy platinum, the gas combines with the oxygen absorbed by the metal, forming water; and this combination is attended with so great a development of heat that the platinum becomes red-hot and causes the ignition of the hydrogen. It is upon this property that the well-known Döbereiner lamp is based. Black platinum is prepared either by boiling sulphate of platinum with carbonate of soda and sugar, when the black platinum is precipitated as a very fine powder, or by melting platinum and zinc together, and treating the alloy with dilute sulphuric acid. Black platinum is industrially employed in the manufacture of vinegar directly from alcohol.

Hammered or Cast Platinum and its Applications. Platinum may be worked by hammering or by casting. The following firms are platinum workers:—Heraeus, at Hanau; Frères Chapuis; Desmoutis and Quennessen, Godart and Labordenave, at Paris; and Messrs. Johnson, Matthey, and Co., London. The chief use of platinum is for various apparatus in chemical laboratories. Although this metal withstands a very high temperature, and is proof against a large number of chemicals which attack or destroy other materials, it requires great care in its use, as it is readily acted upon by caustic alkalies, fusing nitrate of potassa, free chlorine, alkaline sulphurets, phosphorus, molten metals, and readily reducible metallic oxides. Crucibles, spoons, blowpipe points, the points of lightning conductors, tongs and forceps, and boilers for concentrating sulphuric acid are made of this metal. A boiler capable of concentrating daily 8 tons of sulphuric acid costs about £2500, while a smaller but similar vessel for concentrating daily 5 tons of acid costs £1640, the value of the metallic platinum for this size exceeding £1000. Platinum is also used for galvanic apparatus, mustard-spoons, and now and then for ornamental work in watchcases, chains, &c. More recently platinum has been used in porcelain-staining to produce a greyish hue. In the year 1828, the Russian Government commenced coining platinum, 3, 6, and 12 rouble pieces; but by a ukase of 22nd June, 1845, this coinage was discontinued, and the money made, 14,250 kilos. in weight, called in. In France platinum is used for making medals, especially prize medals for exhibitions. The first platinum coin ever made was struck at the Paris Mint in 1799, the dies having been engraved by M. Duvivier with the effigy of the first Consul, afterwards Napoleon I. In the year 1788 there was presented to Louis XVI. a watch, some of the works of which were made of platinum. Small caps or cylinders woven in platinum wire, are used to emit light when rendered highly incandescent by the flame of burning hydrogen, the arrangement being termed a platinum gas lamp. According to M. Kraut, platinum frequently contains barium, or a combination of that metal.

Platinum Alloys. As before observed platinum readily alloys with other metals. Among these alloys, that first made by Deville, consisting of 78·7 platinum and 21·3 iridium, especially deserves notice, as it is not acted upon by nitro-muriatic acid, and is hard and malleable. An alloy of platinum containing 10 to 15 per cent. of iridium withstands fire and reagents far better than platinum alone and is harder; hence the vessels made with it are not so liable to be bent out of shape as those of platinum. According to M. Chapuis, an alloy of 92 parts of platinum, with 5 parts of iridium, and 3 parts of rhodium, resists various reagents better than platinum alone. The alloy of 3 parts of platinum with 13 parts of copper is, according to M. Bolzani, equal in all respects to gold. Dr. Percy states that an alloy of platinum and gold for crucibles and other small vessels applied in chemical operations, is best proof against alkalies. An alloy of equal parts by weight of steel and platinum is the best white speculum-alloy known; its sp. gr. $= 9·862$.

Elayl Platino-Chloride. This compound ($PtC_2H_3Cl_2$) is obtained by repeatedly dissolving chloride of platinum in alcohol, and evaporating the solution to dryness. A very dilute solution when heated on a sheet of glass or a porcelain slate, yields a lustrous coating of platinum

SILVER.

($Ag = 108$; Sp. gr. $= 10·5$ to $10·7$.)

Silver and its Occurrence. Silver is a tolerably abundant metal, and is found partly in the native metallic state, almost always containing gold; partly in combination with other metals, as arsenic, antimony, tellurium, mercury, or combined with sulphur and other sulphurets. Silver rarely occurs as oxide or combined with acids. The chief ores are:—The sulphuret, silver-glance (Ag_2S), containing from 84 to 86 per cent. of silver; the dark-coloured ruby ore ($3Ag_2S + Sb_2S_3$), with 58 to 59 per cent. of silver; the light-coloured ruby ore ($3Ag_2S + As_2S_3$), with 64 to 64·5 per cent. of silver; miargyrite ($Ag_2S + Sb_2S_3$); and the brittle antimonial silver ore ($6Ag_2Sb_2S_3$), with about 67 to 68 per cent. of silver; polybasite [$(Ag_2S,Cu_2S)_9,Sb_2S_3$], with 64 to 72·6 per cent. of silver; and the white ore [$(FeS,ZnS,Cu_2S)_4,Sb_2S_3+(PbS,AgS)_4,Sb_2S_3$], with 30 to 32·69 per cent. of silver. Galena frequently contains silver, usually between 0·01 and 0.03 per cent., and sometimes as much as 0·5 to 1·0 per cent. This lead ore is the chief source of the silver produced in the United Kingdom. Some copper ores contain silver to an amount varying from 0·020 to 1·101 per cent. With regard to zinc ore the reader is referred to the statements under that head.

Extraction of Silver from its Ores. The metallurgical process employed in the extraction of silver may be any of the following:—

- I. By the wet way.
    - 1. By the aid of mercury.
        - *a.* European method of amalgamation.
        - *b.* American method of amalgamation.
    - 2. By means of solution followed by precipitation.
        - *a.* Augustine's method.
        - *b.* Ziervogel's method.
        - *c.* Sundry methods.

II. By the dry way.
1. By concentrating lead ores rich in silver.
2. Separation of the silver from the lead.
   - a. Separation on the hearth.
   - b. Concentrating the silver in the lead by Pattinson's method.
   - c. Eliminating the silver from the lead by means of zinc.
   - d. Refining the silver-glance.

Smelting for Silver Directly.

1. It only rarely happens that silver ores are rich enough to admit of the metal being obtained by a direct smelting process.

Extraction of Silver by Amalgamation.

2. The method of obtaining silver by the aid of mercury, or the amalgamation process, is chiefly applied to very poor ores, and to such metallurgical products as contain only 100 to 120 grms. of silver to the metrical cwt.

European Amalgamation Process.

This process—now obsolete—was conducted in four principal operations—viz., 1. The roasting; 2. Amalgamation; 3. Separation of excess of mercury from the amalgam by mechanical means; 4. Volatilisation of the mercury. There was first added to the ores about 10 per cent. of common salt, and the mixture roasted to volatilise the antimony, arsenic, and other volatile minerals, the fumes being condensed in properly arranged rooms. By the reaction of the common salt upon the pyrites, converted by the roasting into sulphate of iron, there is formed sulphate of soda, chloride of iron, and sulphurous acid, which escapes. The chloride of iron exchanges its chlorine with the silver, the result being the formation of peroxide of iron. There are also formed sulphate of copper and persulphate of iron, which, while oxidising any sulphuret of silver to sulphate, become reduced to protosulphates. By the further action of the common salt, chloride of silver and sulphate of soda are formed, and the other metals converted into chlorides. The brown-coloured mass is next transferred to the amalgamation tuns; and after the addition of water, mercury, and iron, these tuns are made to rotate on their longitudinal axes for a period of 16 to 18 hours, the velocity being regulated to 20 to 22 revolutions per minute. The iron while combining with the chlorine, causes the reduction of all the other metals to the metallic state, and as far as capable these then form an amalgam with mercury.

In order to elucidate the amalgamation process we will, for example, take a silver ore to consist of—

$$(Cu_2S,AgS,FeS) + (As_2S_3,Sb_2,S_3)$$

from which the silver is to be separated, according to the method just described.* After the roasting with common salt (ClNa), there being taken up in this instance 30 mols. of oxygen, the following substances are formed:

$$\underbrace{[(Cu_2Cl_2,AgCl,FeCl_2) + 3Na_2SO_4]}_{\text{Non-volatile substances.}} + \underbrace{[As_2O_3 + Sb_2O_3 + 6SO_2]}_{\text{Volatilised substances.}},$$

The changes which are effected by the action of the iron, mercury, and water in the amalgamation tuns are exhibited by:—

$$[(Cu_2Cl_2AgCl,FeCl_2) + 3Na_2SO_4 + 3Fe + nHg = 3Na_2SO_4 + \underbrace{(Cu,Ag,nHg)}_{\text{Amalgam.}} + 4FeCl_2].$$

At the end of the period destined for the rotation of the tuns, the amalgam is run off. The excess of mercury is strained through a coarse canvas bag, and collected in a stone trough or tank. The real amalgam, a thick pasty mass, remains in the bag, which is next strongly pressed between planks to squeeze out any further excess of non-argentised Mercury. The solid amalgam[*] is then transferred to the iron plates, *bb*, (Fig. 54), arranged as shown in the woodcut, and as already described under the article Mercury. By the action of the fire the mercury is separated from the amalgam, and being volatilised, is collected under the water contained in *d*, while the metallic silver and other metals mixed with it are left on the iron plates.[†]

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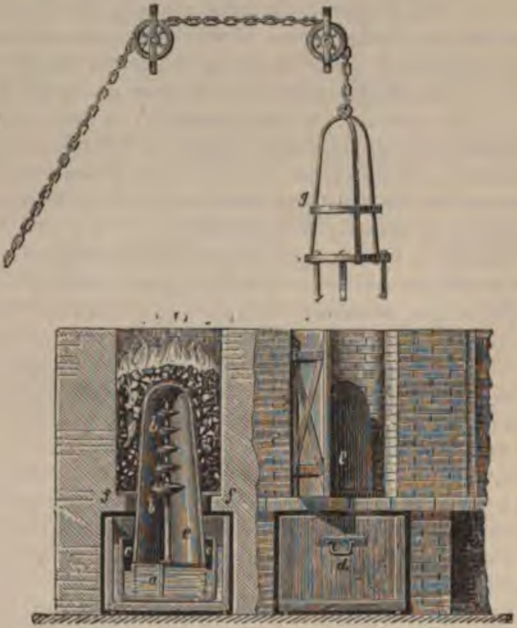
* No attention is paid in this case to the volatile chlorides of sulphur, arsenic, and antimony which are simultaneously formed. The reader who desires more extensive information on the subject here briefly outlined, is referred to Mr. Crookes's "Metallurgy," vol. i.

Fig. 54.



At the present time, instead of the above contrivance, there is used an iron distilling apparatus, not unlike cylindrical iron gas retorts, one end being fitted with a movable lid for the introduction of the amalgam, and the other end connected with an iron tube which dips into a trough filled with water to condense the volatilised mercury. Superheated steam is also advantageously used to separate the mercury from the amalgam. The crude silver left after the separation of the mercury is submitted to a first refining smelting, by being put into graphite crucibles, and the surface covered with charcoal powder. But even after this smelting the silver always contains a certain quantity of copper, from which it can only be separated by refining in a cupel furnace.

American Amalgamation Process.

The American process is chiefly used in Mexico, Peru, Chili, and California. The ores to which it is generally applied are the ruby-silver ores and fahl ores. These are first pulverised in stamping mills, and are next ground with water under granite or porphyry millstones, to a thoroughly impalpable paste. This material is placed in a yard paved with flags, which are laid with a slight inclination sufficient to cause the rain-water to run off. After having been kept there for some days, there is added from ⅓ to 3 per cent. of what the miners locally designate as magistral, that is to say, roasted iron and copper pyrites ($FeCuS_2$), which is thoroughly mixed with the finely-divided ore. Mercury is then added in quantity equivalent to about six times the amount of silver contained in the ore; this operation is termed incorporation. The kneading of the mercury is continued on alternate days for two to five months, and after that time the mass is washed with water in stone cisterns in order to separate the heavy amalgam from the light gangue. The amalgam thus obtained is separated from any excess of mercury by being pressed in canvas bags; the remainder of the mercury being separated by distillation. The *rationale* of this amalgamation process is:--The roasted copper-iron pyrites is essentially made up of mixed sulphates of copper and iron, which when reacting upon the common salt, are converted into chlorides of the metals and sulphate of soda. The chlorides acting upon the silver convert it into chloride, and this becoming dissolved by the excess of salt, is converted by the mercury to the metallic state. Some of the mercury is converted into calomel, and the excess dissolves the silver, becoming amalgamated with it. This American process requires a great length of time, and, moreover, occasions an enormous loss of mercury, as for every mol. of silver reduced from the chloride of that metal there is formed 1 mol. of calomel (Hg_2Cl_2). On the other hand, this method admits of the extraction of silver from ores too poor to be treated in any other way, while a great saving of fuel is obtained.

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[*] According to Dr. Karsten, the composition of the solid amalgam is:—Silver, 11·0; mercury, 84·2; copper, 3·5; lead, 0·1; zinc, 0·2.

[†] The silver left on the plates at the Freiberg mines consists, according to Professor Lampadius, of:—Silver, 75·0; mercury, 0·7; copper, 21·2; lead, 1·5. The refined silver of the same place contains, according to Professor Plattner:—Silver, 71·55; copper, 28·01.

Augustin's Method of Silver Extraction. This hydrometallurgical method, invented by M. Augustin, is based upon the formation of a soluble double chloride of silver and sodium when chloride of silver is treated with an excess of a warm solution of common salt, and also upon the fact that copper is capable of precipitating all the silver from this solution. The ore is first reduced to a finely-divided powder, which essentially contains sulphurets of copper, silver, and iron. This powder is roasted, first without the addition of common salt, with the result that sulphates of the metals are formed, and excepting that of silver, again decomposed by a higher temperature. The mass is next roasted with common salt, whereby the sulphate of silver is converted into chloride. The mass is then treated with a concentrated hot solution of common salt, which dissolves the chloride of silver, and from this solution the silver is precipitated by metallic copper, which becomes chloride of copper, and is, in its turn, precipitated by metallic iron.

Ziervogel's Method. This method is to some extent similar to that just described, but no roasting with common salt takes place. The roasted ore, chiefly containing as essential ingredients sulphate of copper and sulphate of silver, is treated with boiling water to dissolve these sulphates, and yield a solution from which metallic silver is precipitated by means of copper, the sulphate of that metal being obtained as a by-product. When the ores happen to contain arsenic and antimony, this method is not applicable, as, by the roasting, arseniate and antimoniate of silver are formed, which are insoluble in water. If lead is present, the ore becomes fluxed and the roasting a far more difficult matter.

Sundry Hydrometallurgical Methods of Extracting Silver. Dr. Carl Ritter von Hauer suggests the treatment of the ores as in the European amalgamation process, and the extraction of the chloride of silver by means of a hyposulphite of soda solution, the metallic silver being next precipitated by the aid of copper or tin. Dr. Patera suggests the substitution in Augustin's method of a hyposulphite of soda solution for that of common salt. the former being more manageable and applicable cold. Similar suggestions have been made by Dr. Percy, who also advocates the applicability of hypochlorite of lime, and of chlorine gas for converting the silver into chloride. MM. Rivero and Gmelin were the first to suggest the use of ammonia for the purpose of extracting and dissolving the chloride of silver after the ores had been roasted with common salt; the precipitation of the chloride from the ammoniacal solution by means of sulphuric acid, and the smelting of the chloride with a suitable flux to obtain metallic silver. We must not omit to mention the method of extracting silver from copper regulus and mattes by means of hot dilute sulphuric acid, whereby the copper is dissolved and a residue left containing the silver, which is further extracted in the dry way by means of lead.

Extraction of Silver by the Dry Way. The method of extracting silver from its ores by means of lead is based upon:—

1. The property of lead to decompose sulphuret of silver, with the formation of sulphuret of lead and metallic silver; $\left.\begin{array}{l} Ag_2S \\ nPb \end{array}\right\}$ yield $\left\{\begin{array}{l} Ag_2Pbn \\ PbS. \end{array}\right.$

As lead hardly acts at all upon the other metallic sulphides, and least of all upon those of copper and iron, the products of the smelting are lead combined with silver, and a regulus consisting of the sulphurets of lead, copper, and iron. This method of extraction succeeds best with ores containing as small a quantity of copper as possible.

2. Upon the decomposing reaction exerted by oxide of lead and sulphate of lead upon the sulphuret of silver, in consequence of which there are formed metallic lead containing silver and sulphurous acid:—

$$\left.\begin{array}{l} Ag_2S \\ 2PbO \end{array}\right\} \text{yield} \left\{\begin{array}{l} Pb_2Ag_2 \\ SO_2 \end{array}\right.$$

and

$$\left.\begin{array}{l} Ag_2S \\ PbSO_4 \end{array}\right\} \text{yield} \left\{\begin{array}{l} PbAg_2 \\ 2SO_2 \end{array}\right.$$

3. Upon the reducing action of lead upon oxide of silver or upon sulphate of silver:—

$$\left.\begin{array}{l} 2Pb \\ Ag_2O \end{array}\right\} \text{yield} \left\{\begin{array}{l} PbO \\ Ag_2Pb \end{array}\right.$$

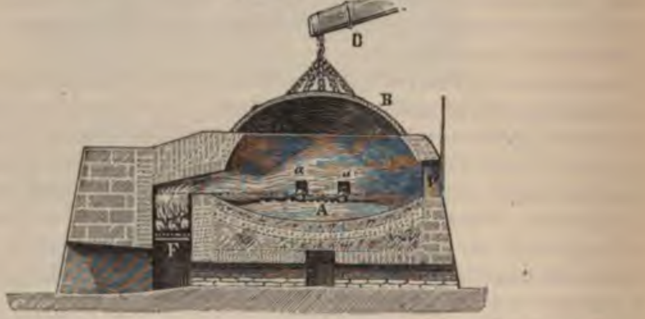
and

$$\left.\begin{array}{l} 3Pb \\ Ag2SO_4 \end{array}\right\} \text{yield} \left\{\begin{array}{l} PbAg \\ 2PbO \\ 2SO_2 \end{array}\right.$$

4. Upon the greater affinity of the silver for lead than for copper. If copper that contains silver is melted with lead, the result is the formation of a readily fusible alloy of lead and a difficultly fusible alloy of copper and lead, the former metal being separable by liquation.

Mode of preparing the Lead-containing Silver. Only genuine silver ores are submitted to the operation of smelting with lead, but these ores usually contain variable proportions of copper, lead, cobalt, sulphur, and other substances. The result of the smelting with lead is the production of a metal containing silver, to be separated by any of the following operations:—

Fig. 55.



1. On the refining-furnace;
2. By Pattinson's process;
3. By means of zinc.

Refining Process. This operation is as frequently carried on at lead-ore smelting-works as where only silver is smelted. The *rationale* of the operation is that lead is readily separated from such metals as are at a high temperature either oxidisable with very great difficulty or not at all; whereas lead oxidises readily, its oxide becoming fluid. But it is requisite that the oxide of lead should be removed or absorbed by a suitable medium, generally the porous substance composing the cupel or bottom of the hearth of the refining furnace. The operation is carried on as long as any oxide and metallic lead remain, so that only the silver is left. This operation is the exact counterpart on the large scale of the well-known lead-silver assay carried on in a muffle with bone-ash cupels. The refining furnace, see Fig. 55, is a circular reverberatory blast-furnace. The hearth, A, is covered with a dome of stout sheet-iron, lined inside with fire-clay, and removable by means of a crane, D. That portion of the hearth upon which the smelting is carried on is constructed of a porous substance, generally lixiviated wood-ash or marl of good quality. The cavity, c, is intended for collecting the silver; B is the space for the flame. In the circular wall which surrounds the hearth there are:—(1). The door, not exhibited in the cut, which represents a vertical section intended for the discharge of the molten litharge. At the outset of the smelting this door is only partly closed with fire-clay to admit of the litharge being run off. The furnace is charged with lead to a little above the level of the lower sill of this door, and the fire-clay gradually removed as the level of the fused litharge sinks. (2). The door, P, opposite to the fire-place, and intended for the charging and construction of the hearth. (3). The openings, *a a'*, admitting the tuyeres of the blast.

The refining operation is carried on at a gradually increased temperature until only a very thin layer of oxide of lead covers the surface of the silver. This is known by the peculiar display of colours, technically known as the *brightening*, more aptly expressed in German by a word which means *lightening*, for that is really the appearance. This being observed, the fire is slackened, and the silver having been cooled with water, is removed from the hearth. The litharge which runs off is, on cooling, a yellow or reddish-yellow crystalline mass (see Lead, p. 63).

Pattinson's Method. The refining process just described is not suited, that is to say, does not pay, when the lead contains only 0·12 per cent. of silver. Now it so happens that the various kinds of galena met with in England yield a lead which contains only 0·03 to 0·05 per cent. of silver. In 1833, Mr. H. L. Pattinson, of the Felling Chemical Works, near Gateshead-on-Tyne, instituted a series of experiments relative to a new method, applicable on the large scale, for separating lead from silver when the latter is present in small quantities. His efforts were successful, and have greatly benefited his own and other countries where his process is worked.

Pattinson's method essentially consists in a concentration process, based upon the phenomenon that when a certain quantity of lead that contains silver is melted in iron cauldrons, and the fluid mass allowed to cool uniformly, there ensues a formation of small octahedral crystals which do not contain any silver at all, or, at any rate, are a great deal poorer in silver than the metal originally taken, while the portion of the metal remaining fluid is found to contain an increased quantity of silver. It is clear, therefore, that if the crystals first obtained are again melted and cooled uniformly, another concentration will be obtained, and that the operation can be repeated until a lead is obtained rich enough in silver to admit of undergoing a refining process. Practically, Mr. Pattinson's method admits of concentrating 2·5 per cent. of silver. In the execution of this process, the ⅔ and ⅞ systems are employed. If the first, at every operation two-thirds of the contents of the cauldron are removed with perforated ladles, while in the other case, seven-eighths is the quantity of crystals ladled out, leaving respectively one-third and one-eighth of the contents of the cauldron in the shape of fluid lead. The ⅔ system is better suited for the richer lead, the ⅞ system for very poor lead. M. Boudchen has recently modified Pattinson's process. Instead of ladling out the crystals, he diffuses them in the lead, and stirs them about to prevent them enclosing any lead likely to contain silver. The lead is withdrawn from the cauldron by means of a tap at the bottom. In all cases, however, the quantity of lead operated on at one time is always large, generally 200 cwts., to cause the cooling to proceed slowly. At the Freidrich Lead Silver Works, near Tarnowitz, the enriched lead contains 1·28 per cent. of silver.

Reduction by Means of Zinc. This process, suggested by Mr. Parker, in 1850, has only recently been practically carried out by M. Cordurié, at Toulouse. This method, as far as we are now capable of judging, will probably supersede even Pattinson's excellent method. The *rationale* of the process is based upon the facts :—1. That lead and zinc do not alloy together. 2. That the affinity of silver for zinc is much greater than for lead.

The following is the manner of execution :—20 cwts. of lead, which may contain (per ton) only 0·25 kilo. of silver, is melted, and when properly liquefied there is added 1 cwt. of molten zinc. The zinc having been thoroughly mixed with the lead, the molten mass is left to stand until the zinc, which has risen to the surface, forms a cake that is easily removed. The zinc is then separated from the silver by distillation. The residue of the distillation is melted with lead, and the alloy thus obtained refined as above described. The zinc obtained by the distillation is used for another operation. According to a more recent improvement, the zinc is separated from the silver by oxidation by passing superheated steam over the red-hot zinc ($Zn + H_2O = ZnO + H_2$). The lead, which of course after this operation contains traces of zinc, is purified by being melted with either chloride of lead, or a mixture of sulphate of lead and chloride of sodium, or with chloride of potassium from Stassfurt, the result being the formation of chloride of zinc, which collects at the surface or may be volatilised at a low red heat.

The Ultimate Refining of Silver. In whatever manner silver may have been metallurgically obtained, the metal is a crude material, very far from being cent-per-cent silver. The impurities, foreign metals, or, more correctly, base metals, often amount to 7 and even 8 per cent.; and in order to remove these, the silver is submitted to a process of ignition in, or rather on the surface of, vessels made of an absorbent material. This material is, for this ultimate refining, generally bone-ash, which is pressed into iron rings of convenient size, care being taken to fuse some lead with the silver, if there is not already sufficient. As regards this ultimate refining, there can be distinguished three different methods. The first has just been described. The second is carried on in muffles, the base metals burning off slowly. The third, and most advantageous method, is carried on in a reverberatory furnace. 100 parts of crude silver yield 96·8 parts of refined silver at 99·9 per cent. pure fine metal, which is cast in large-sized bars. The value of the annual production of fine silver amounts to £9,000,000. Of this, Mexico's share is the largest, being half of the entire production. The bulk of this silver contains some gold and platinum.

Chemically Pure Silver. When for certain purposes metallic silver is required chemically pure, it may be obtained by dissolving any ordinary silver coin in nitric acid, and precipitating the solution with an aqueous solution of common salt or hydrochloric acid. The chloride of silver thus obtained should be reduced by ignition in a crucible with dry carbonate of potassa, to which a little resin may be added. But chloride of silver is now commonly reduced by the wet way, by causing it to be acted upon by metallic zinc and a dilute solution of either sulphuric or hydrochloric acid.

$$(2AgCl + Zn + ClH = ZnCl_2 + Ag_2 + ClH).$$

Properties of Silver. Silver obtained by smelting exhibits a pure white colour and a strong metallic lustre, which is greatly increased by polishing. Its fracture is compact rather than fibrous. It is softer than copper, but harder than pure gold; when chemically pure its softness is greatest. It is not a sonorous metal, bearing a resemblance in this respect to tin and lead. Gold only excepted, silver is the most ductile of the metals, a property impaired by the presence of foreign metals other than copper and gold, by the latter of which the ductility is slightly increased. Lead and antimony render silver brittle. When silver contains an excess of carburet, produced by smelting the metal with an excess of carbon, the metal is rendered less ductile; but a small quantity of the carburet, as much as is found in coins of a high percentage of silver, is rather advantageous, increasing the hardness of the metal, and causing it to wear well. Smelting in plumbago crucibles does injure silver. Its specific gravity varies from 10·5 to 10·7. The absolute strength is far less than that of copper. Its expansion by heat in 0° to 100° C. is $\frac{1}{524}$th. According to M. Deville, the melting-point is 916°; but Dr. van Riemsdijk states that the results of a series of experiments made at the Utrecht Mint in 1868, showed the melting-point to be 1040°, the metal being kept in a slow current of pure hydrogen. At a very high temperature, such as can be produced only by the oxyhydrogen flame or by electricity, silver is volatilised. When alloyed to other metals, especially to copper, the volatility is increased, and even at a lower temperature than the melting-point of copper, viz., 1330°, Dr. van Riemsdijk found such silver to be perceptibly volatile. M. Stas, of the Brussels Mint, in 1869, distilled some 50 grms. of silver by means of the oxyhydrogen flame, in order to obtain the metal perfectly pure. Molten silver absorbs oxygen, which is again expelled from the metal on solidification, and gives rise to the phenomenon known by silver-assayers as spirting, the escape of the gas causing the metal to be forced asunder in small drops. However, when the molten silver contains even 1 per cent. of either lead or copper, it solidifies without spirting. Silver is not acted upon by dilute acids, but is readily dissolved in the cold by nitric acid. Silver is very sensitive to the action of sulphuretted hydrogen, by which it is readily tarnished.

Alloys of Silver. Silver alloys readily with lead, zinc, bismuth, tin, copper, and gold; but the most important alloy, in an industrial point of view, is that with copper, pure silver being too soft for general application. All silver, therefore, whether used for plate, coin, or for ornamental purposes, invariably contains a certain amount of copper. In most civilized countries there exist laws regulating the alloy of silver to be used for coin or plate. Pure silver, or fine silver, is now generally indicated by $\frac{1000}{1000}$. The alloy for the silver coins of Germany is indicated by $\frac{900}{1000}$; meaning that 1000 parts by weight of the coin contain 900 parts of pure silver, the remainder being copper. Twenty-seven Union thalers weigh 1 half kilo., therefore a single thaler weighs 18·518 grms., and contains 16·666 grms. of pure silver. By an international treaty with France, Italy, Belgium, Portugal, Switzerland, and Spain, 1 kilo. of $\frac{900}{1000}$ silver is to yield 200 franc pieces, *i.e.*, 222$\frac{2}{9}$ franc pieces to 1 kilo. of *fine* silver. The same alloy is employed for pieces of 2 and 5 francs, there being 200 of the latter to the kilo. In the Netherlands, where, by-the-bye, gold coin is no longer current, and silver is the standard, the alloy used is $\frac{945}{1000}$. The silver coins of the United Kingdom are made of an alloy $\frac{925}{1000}$; 1 lb. Troy, or 373·228 grms., of this alloy is coined into 66 shilling pieces. A pound Troy of fine silver would yield 71$\frac{13}{37}$ shillings.

Silver Alloy for Plate, &c. In nearly all European countries the laws have fixed the composition of the alloy of silver which, duly marked and stamped, shall be offered for sale as plate by gold- and silver-smiths, who, in Holland, Belgium, France, and Sweden, are not allowed to have in their workshops any electro-plated articles, or any alloys other than those fixed by law. The composition of these alloys varies; expressed in millièmes of fine metal, it is for Austria and Bavaria, 812; for Prussia and Saxony, 750; for England, 925. For France, Belgium, and the Netherlands, a double alloy is fixed, the higher being 950, the lower 800. The alloy lately brought into use under the name of *tiers-argent*, one-third silver, really consists of 27·56 per cent. silver, 59 per cent. copper, 9·57 per cent. zinc, and 3·42 per cent. nickel, though in the trade this alloy is alleged to consist of $\frac{2}{3}$ nickel and $\frac{1}{3}$ silver. *Tiers-argent* sells at £3 12s. per kilo. This alloy is harder than silver; its colour and polish are as good. It is extremely well adapted for all kinds of plate.

Silver Assay. If it be desired to know the quantity of fine silver contained in an alloy of silver—which for our present purpose we will assume to contain only silver and copper—there are three different methods by which this proposition can be solved, viz.:—1. The assay by the dry way, termed cupellation. 2. The assay by the wet way, or titration process. 3. The hydrostatic assay.

Dry Assay. Usually this assay is conducted by first testing the alloy by comparing the streak it makes upon touchstone—a piece of polished basalt or siliceous schist—with the streak produced upon the same stone by test-needles; that is to say, small bars of silver of known composition. It should, however, be borne in mind that the surface of silver articles, as well as of coins, may have been *blanched*, as the term runs; that is to say, acted upon by hot, dilute sulphuric acid, to dissolve a portion of the copper of the alloy, and leave a film of alloy richer in silver. The alloy to be further assayed is next melted down with a piece of pure soft lead, or lead containing a known quantity of silver, in a capsule, technically called cupel, made of bone-ash. The cupel is previously well heated in a muffle, and the lead is placed in it. As soon as the lead has become quite liquid, the sample of silver to be assayed is added; the copper and lead are oxidised, and in that state absorbed by the porous substances of the cupel. As soon as the surface of the silver button appears quite bright, the operation is finished, and the cupel slowly cooled. The button of silver is then weighed. It is usual to make two assays of the same sample; these assays should agree in their results to within $\frac{1}{1152}$nd to be of any value.

Wet Assay. This method of assaying silver was devised some sixty years ago by the late Professor Gay-Lussac, at the request of the French Government, in consequence of the great irregularity of the results obtained by the dry method. The wet assay, having been very greatly improved in detail by Dr. G. J. Mulder, M. A. W. H. van Riemsdijk, Dr. Stas, and M. J. Dumas, is now generally adopted, and will remain to all time a masterpiece worthy of the ingenuity of its original inventor, who, by introducing this method, laid the foundation of volumetric analysis, now so usefully and completely applied. Gay-Lussac's wet method of silver assay is more easily executed than the dry assay, while it is far more correct, admitting an accuracy of judgment within $\frac{1}{20}$th per cent. The method is based upon the property possessed by common salt of precipitating silver as chloride of silver from its nitric acid solution. As 5·4274 grms. of pure common salt exactly convert 1 grm. of pure silver, previously dissolved in nitric acid, into chloride of silver, it is evident that, from these data, and with the application of suitably constructed apparatus for the volumetric analysis, the fineness of any alloy of silver may be ascertained readily, rapidly, and with great accuracy.

Hydrostatical Assay. This method is of course by no means so correct as either of the foregoing, and, moreover, is impaired by the fact that, although alloys of copper and silver expand under pressure, they become denser, so that the hydrostatic weighing, that is to say, the estimation of the specific gravity of the alloy, is only admitted as a test of its relative value. With such alloys as have, like coins, to be rolled, pressed, or drawn, the hydrostatical results rarely differ more than $\frac{10{\cdot}4}{1000}$ from the results obtained by cupellation. The empirical rule for the estimation of the value of silver assayed by this method is the following:—The number 8·814 is subtracted from the specific gravity of the alloy, two cyphers are added to the difference, and the figure thus formed, considered as a whole number, is divided by 579; the quotient is the fineness of the silver alloy expressed in grains. For instance, let the specific gravity of the alloy be $=$ 10·065, then the fineness is $=$ 216 grains, or $\frac{750}{1000}$; since—

$$10{\cdot}065 - 8{\cdot}814 = 1{\cdot}251$$

and

$$\frac{125{,}100}{579} = 216$$

Silvering. The coating of metals with a film of silver can be effected by:—1, plating; 2, the igneous process; 3, in the cold; 4, the wet way; 5, galvanically, or electro-plating.

Silver-Plating. In order to coat metallic copper with a layer of silver, the sheet copper is first thoroughly cleansed, then treated with a moderately strong solution of nitrate of silver, and next covered with a sheet of silver. After having been made red-hot, the two metals are rolled out together. The silver then adheres so strongly to the copper as to admit of the metals being beaten or stamped into various shapes. Copper-wire is readily silvered by being covered with thin strips of silver, and passed through rollers. But this method of plating is almost entirely superseded by electro-plating.

Igneous, or Fire-Silvering. This method of silvering is effected by the aid either of a silver-amalgam, or by applying to the well-cleansed surface of the metal intended to be silvered a mixture of 1 part of spongy precipitated metallic silver, 4 parts sal-ammoniac, 4 parts common salt, and $\frac{1}{2}$ part corrosive sublimate. The metal to be silvered is rubbed with this mixture, and then heated in a muffle. Buttons intended to be silvered are covered with a paste consisting of 48 parts of common salt, 48 parts sulphate of zinc, 1 part of mercuric chloride, and 2 parts of chloride of silver.

Silvering in the Cold. The metallic surface intended to be silvered, having been well cleaned, is rubbed by means of a smooth cork, with a mixture of equal parts of chloride of silver, common salt, $\frac{2}{3}$ of chalk, and 2 of carbonate of potash, made with water into a creamy paste. Professor Hein recommends that 1 part of nitrate of silver and 3 of cyanide of potassium should be rubbed together in a mortar, with the addition of sufficient water to form a thick paste. The paste is rubbed on the metal to be silvered with a piece of flannel. MM. Roseleur and Lavaux recommended a mixture of 100 parts of sulphite of soda and 15 parts of any salt of silver. For silvering the dial-plates of watches, &c., M. Thiede recommends a mixture of spongy silver with equal parts of common salt and cream of tartar. In order to silver iron it is first covered with a layer of copper.

Silvering by the Wet Way. This is effected by immersing the metal intended to be silvered in a boiling aqueous solution of equal parts of cream of tartar and common salt, with ¼ part of chloride of silver. The description of the methods of electro-plating will be given at the end of the chapter on Metals.

Oxidised Silver. The small ornaments met with under the name of oxidised silver are prepared with either sulphur or chlorine; in the former case a bluish-black colour is imparted, in the latter a brown. The sulphur is applied simply by dipping the object into a solution of sulphuret of potassium, while for the chlorine colour a mixture of sulphate of copper and sal-ammoniac is used.

Nitrate of Silver. This salt ($AgNO_3$) is now prepared on the large scale by dissolving silver containing copper in nitric acid, evaporating the solution to dryness, and igniting the residue until all the nitrate of copper is decomposed. The residue is next exhausted with pure water, the solution filtered and left to crystallise. For medical purposes the crystals are fused, and while liquid poured into moulds to form small round sticks. The most extensive use of nitrate of silver obtains in photography, a re-crystallised neutral and pure salt being preferred. Under the name of *Sel Clément*, there is now in use in photography a mixture of fused nitrates of silver, sodium, and magnesium, recommended as preferable to nitrate of silver alone. It is stated that the consumption of this salt for photographic purposes amounted, in 1870, to 1400 cwts. for Germany, France, England, and the United States; the money value of this quantity being estimated at £630,000.

Marking Ink. A large quantity of nitrate of silver is also used for the purpose of making indelible ink for marking linen. This ink often consists of two different fluids, one a solution of pyrogallic acid in a mixture of water and alcohol, being intended to moisten the linen previous to writing; the other, or writing fluid, consisting of a solution of ammoniacal nitrate of silver thickened with gum. More recently aniline black has been applied in the marking of linen.

GOLD.

(Au = 197; Sp. gr. 19·5 to 19·6.)

Occurrence and Mode of Extracting Gold. Gold is found only in the native metallic state, sometimes in veins interspersed in rocks, and accompanied by quartz, iron pyrites, and iron ore. More frequently gold is found finely divided in sand, mixed with larger or smaller nuggets, and imbedded in quartz, with various other minerals, such as mica, syenite, chlorite slate, chrome-iron ore, and spinel. Native gold commonly contains some silver and other metals, among which are palladium and platinum. According to recent analyses, the composition of samples of gold obtained from several countries is:—

					I.	II.
	Hungary.	S. America.	Siberia.	California.	Australia.	
Gold . . .	64·77	88·04	86·50	89·60	99·2	95·7
Silver . . .	35·23	11·96	13·20	10·06	0·43	3·9
Iron and other metals	—	—	0·30	0·34	0·28	0·2

Gold is found native with tellurium and telluride of silver, and among antimony, zinc, arsenic, and other ores. It is also found in galena and various kinds of clay; indeed, gold is, next to iron, the most widely dispersed metal. The chief gold-yielding countries are:—Africa, Hungary, the Oural, Australia, and America, especially Mexico, Peru, the Brazils, California, Columbia, and Victoria.

The total value of the gold produced in the year 1869 is computed at £60,000,000, one-fourth of this representing the value of the production of California. The value of the joint production of the Australian Colonies is a little above another one-fourth.

Mode of Extracting Gold. The mode of extracting gold is determined by the circumstances of its occurrence. By far the largest portion of the gold in circulation is obtained by the washing process; that is to say, the elimination by means of water of the lighter minerals, the finely-divided gold being left behind. This process may be carried on in remote districts in a very primitive manner, by simply putting the sand into wooden bowls, and washing it gradually away with water. The gold so obtained is not pure, but contains titanic iron and other minerals. Wherever gold washing is a regularly established business, as in some parts of the Oural, properly constructed contrivances are applied.

Extraction by means of Mercury. The application of mercury to the extraction of gold is based upon the fact that mercury amalgamates with gold readily and very effectively. The operation is carried on with the gold-containing sand in peculiarly constructed mills. Mr. Crookes has shown that the addition of sodium to the mercury facilitates the extraction of the gold. The excess of mercury having been removed from the amalgam by pressure in leathern or stout linen bags, the remainder in amalgamation with the gold is volatilised by ignition in suitably constructed furnaces.

Smelting for Gold. By a far more perfect process than washing, gold is extracted from the gold sand by smelting with a suitable flux in a blast furnace. The object in view is to produce a rough or crude iron from which the gold is separated by means of sulphuric acid. This process yields from 25 to 30 times more gold than merely washing the sand.

Treating with Alkali. Mr. Hardings proposed to obtain the gold by treating the quartz or sand with caustic alkalies under a high pressure of steam, thereby forming a soluble silicate and leaving the gold.

Extraction of Gold from other Metallic Ores. If gold happens to be interspersed through copper or lead ores, they are roasted and then washed. When the quantity of gold is sufficient such ores are treated with mercury, while sometimes they are treated for coarse metal; and this, containing all the gold, is smelted with litharge, which absorbs the gold, and is next separated from it on a refining hearth.

Extraction of Gold from Poor Minerals. Some minerals and metallurgical refuse containing only a very small quantity of gold have been treated at Reichenstein, in Silesia, by means of chlorine water, or an acidulated solution of bleaching powder. The gold is converted into chloride of gold ($AuCl_3$), and is precipitated from the solution by sulphate of iron or sulphuretted hydrogen. This method has been severely tested by MM. Plattner, Th. Richter, Georgi, and Dr. Duflos, and has been found to answer exceedingly well, even with very poor ores. This plan is of course generally applicable to gold sand and gold quartz. According to M. Allain, pyritical ores, having been roasted and treated with sulphuric acid to eliminate the iron, zinc, and copper, can be then treated with chlorine water so as to extract the gold present, to an amount only of 1 part of gold in 10,000 of mineral.

Refining Gold. In order to separate any foreign metals from the gold obtained by the above process, the following methods have been employed, but only the last (5.) is now in general use. For that reason the other methods will only be briefly described:—

1. Refining by means of sulphuret of antimony (Sb_2S_3).
2. By means of sulphur and litharge.
3. By cementation.
4. By quartation.
5. By means of sulphuric acid.

By means of Sulphuret of Antimony. This process is effected by first smelting the alloy, which ought to contain at least 60 per cent. of gold, in a graphite crucible. Pulverised black sulphuret of antimony is added in the proportion of 2 parts to 1 of alloy, and the molten mass is then poured into an iron mould, which is rubbed with oil. The mass on cooling will be found to consist of two separate layers—the upper, technically termed *plagma*, consisting of the sulphurets of silver, copper, and antimony; the lower, an alloy of antimony and gold, which is separated in a muffle or a wind furnace. The remaining gold is fused with borax, saltpetre, and some powdered glass.

By the aid of Sulphur. This process does not aim at the entire separation of the gold from the other metals, but rather at its concentration in a smaller quantity of silver than was originally present in the alloy, so as to render it suited for quartation. The alloy, previously granulated, is mixed with ¼ part of powdered sulphur, put into a red-hot graphite crucible, and covered with charcoal powder. The crucible is kept at a low red heat for 2½ hours, and then raised to the point of fusion. If the alloy contained gold in any considerable quantity, a layer of silver separates, which will be rich in gold, but if the original alloy was rather poor in gold, litharge is added to the molten mass, the oxygen of the litharge causing the combustion of the sulphur of a portion of the sulphuret of silver, the metallic silver combining with nearly all the gold. The reduced lead is taken up by the sulphurets of the other metals present.

Cementation Process. The alloy containing gold having been either granulated or rolled into thin sheets suitably cut up, is placed in a crucible, in this instance technically termed a cementation box, and mixed with 4 parts of pulverised bricks, and 1 part each of common salt and dried copperas. The crucible is then gradually raised to a cherry-red heat. Chlorine is evolved in this operation by the action of the sulphate of iron upon the common salt; there is consequently formed chloride of silver, which is absorbed by the pulverised bricks, while the gold is left unattacked. After cooling, the mass is boiled in water in order to obtain the gold. Here must be mentioned Mr. F. B. Miller's process of passing chlorine into molten gold in order to eliminate the base metals which render it brittle, while the silver, converted into chloride, floats to the surface.

Quartation. This process has obtained its name from an opinion that, to ensure success, there should be three times more silver in the alloy than gold, *i.e.*, the gold should amount to a quarter of the entire alloy. But Dr. M. von Pettenkofer has proved that if the amount of silver be double that of the gold, the separation of the two metals will be complete, provided sufficiently strong nitric acid be employed, and the boiling continued for a length of time. Practically this method is as follows:—There is added to the gold a sufficient quantity of silver, and the two metals are smelted together. The alloy is next granulated, placed in a platinum vessel, and boiled with nitric acid of 1·320 sp. gr., care being taken that the acid is free from any chlorine. The silver being dissolved, the gold is left behind, and further refined by fusion with borax and saltpetre in a crucible.

Refining Gold by the Aid of Sulphuric Acid. This method of refining, which has been briefly alluded to under Copper, is preferable to any of the foregoing on account of its perfection, cheapness, and simplicity. By this method almost any alloy containing gold in addition to copper and silver can be treated, but the quantity of gold should not exceed 20 per cent., nor that of the copper 10 per cent., while the best proportions, according to Dr. Pettenkofer's researches are, that in 16 parts of the alloy, the gold should not exceed 4 or be much less than 3 parts, and the rest copper and silver. Usually the alloy intended for this mode of operation is first granulated, or if it happens to be in the shape of silver coins—Mexican dollars, for instance—they are cut to pieces. Formerly, platinum vessels were employed in the boiling of the alloy with thoroughly concentrated sulphuric acid (sp. gr. 1·848), but cast-iron vessels, or sometimes hard porcelain vessels, are now employed, the proportion being 2 molecules of acid to 1 molecule of the alloy. The heating is continued some twelve hours, until the copper and silver are completely dissolved. The sulphurous acid evolved is employed in the manufacture of sulphuric acid, or is absorbed by a soda or lime solution to form sulphite or bisulphite of soda or bisulphite of lime. The solution of mixed sulphates of silver and copper is poured into leaden pans, and becoming solidified on cooling, the pasty mass is dug out with iron spades, and put into leaden tanks filled with boiling water, in 88 parts of which 1 part of sulphate of silver is soluble. The silver is precipitated from this solution by strips of copper, and the solution of sulphate of copper obtained, having been deprived of its excess of free acid by the addition of oxide of copper, is further treated for blue vitriol. The gold which has remained as a dark, insoluble, spongy mass, is first boiled with a solution of carbonate of soda, next with nitric acid, to free it from any adhering oxide of iron, sulphuret of copper, sulphate of lead, and other impurities; and after having been dried, is melted with the addition of saltpetre. By this process it has become possible to extract the 1-10th to 1-12th per cent. of gold contained in old silver coins; therefore this method of refining has come largely into use, as within the last thirty years nearly all European States have recoined the silver money in circulation. Still Dr. von Pettenkofer has observed, that nearly all the gold obtained by this process contains silver and platinum, in the proportion of 97·0 gold, 2·8 silver, and 0·2 platinum. These metals are eliminated by fusion with saltpetre and bi-sulphate of soda.

At Paris, Frankfort, London, and Amsterdam, this method of refining is carried on to a large extent by private firms. According to the Paris custom, the refiners return to their clients all the silver and gold, retaining only the copper, and being paid at the rate of from 5 to 5½ francs per kilo. of refined metal; but if the alloy contains less than 1-10th of gold, the refiners retain 1-2000th of that metal, paying a premium of ¾ franc per kilo. of refined metal to their client. If the client desires all the gold and silver to be returned to him, the refiner charges 2 francs and 10 to 68 centimes per kilo., according to the market price of silver, and retains all the copper. Usually, however, a charge of 5 francs per kilo. is paid to the refiner. The value of the silver annually refined for gold, at and near Paris, amounts to about £5,500,000.

Chemically Pure Gold. In order to obtain perfectly pure gold, that of commerce is dissolved in nitro-hydrochloric acid, the solution evaporated to dryness, the residue, chloride of gold, dissolved in water, and that solution precipitated by a solution of sulphate of iron :—

$$\left.\begin{array}{l}\text{Chloride of gold, } 2(AuCl_3)\\ \text{Sulphate of iron, } 6FeSO_4\end{array}\right\}\quad\text{yield}\quad\left\{\begin{array}{l}\text{Gold, } 2Au.\\ \text{Persulphate of iron, } 2Fe_23SO_4.\\ \text{Chloride of iron, } Fe_2Cl6.\end{array}\right.$$

According to Mr. Jackson, gold may be readily obtained in a yellow spongy mass, by adding carbonate of potassa and an excess of oxalic acid, to a concentrated solution of chloride of gold, and rapidly heating this solution to the boiling-point :—

$$\left.\begin{array}{l}\text{Chloride of gold, } 2(AuCl_3)\\ \text{Oxalic acid, } 3C_2H_2O_4\end{array}\right\}\quad\text{yield}\quad\left\{\begin{array}{l}\text{Gold, } 2Au.\\ \text{Hydrochloric acid, } 6ClH.\\ \text{Carbonic acid, } 6CO_2.\end{array}\right.$$

According to Mr. Reynolds, peroxide of hydrogen precipitates gold from its acid solution in beautifully lustrous metallic spangles :—

$$\left.\begin{array}{l}\text{Chloride of gold, } 2(AuCl_3)\\ \text{Peroxide of hydrogen, } 3H_2O_2\end{array}\right\}\quad\text{yield}\quad\left\{\begin{array}{l}\text{Gold, } 2Au.\\ \text{Hydrochloric acid, } 6ClH.\\ \text{Oxygen, } 6O.\end{array}\right.$$

Sometimes gold is precipitated by chloride of antimony or chloride of arsenic. The metallic gold obtained or precipitated by any of the above processes is next fused with borax in a graphite crucible.

Properties of Gold. The peculiar colour of gold is too well known to require description. The richness of that colour is very much impaired by even small quantities of other metals. Many of the Australian sovereigns, for instance, are of a pale greenish yellow, due to the presence of a small quantity of silver. A small quantity of copper gives a red colour to the gold. Gold assumes a very high polish; is, when unalloyed, but slightly harder than lead, and yet is the most malleable and ductile of all metals. Its absolute strength is equal to that of silver. The specific gravity of gold varies from 19·25 to 19·55, and even 19·6, according to the mode of mechanical treatment. Its co-efficient of expansion by heat = 682 per 100° C., and its melting-point, according to Dr. Deville, is 1037°. Dr. Van Riemsdijk, however, fixes the melting-point at 1240°, the metal being molten in quantities of several kilos. in an atmosphere of pure dry hydrogen. Molten gold exhibits a sea-green colour. The great value of gold is in a considerable measure due to its not being acted upon by air, water, ordinary acids, and alkalies; but, on the other hand, even very small quantities of lead, antimony, and bismuth impair its malleability to such an extent as to render it unfit for use either as coin or for ornamental purposes. The following metals have the same effect, but to a less extent: arsenic, zinc, nickel, tin, platinum, copper, and silver; the two latter being the only metals suitable to alloy with gold to make it sufficiently hard to resist wear and tear. Gold, of all the metals, is most readily affected by mercury, even to such an extent that the mercury present in the imperceptible perspiration of such individuals as have been treated medicinally with calomel for some length of time, is sufficient to act very perceptibly upon their jewellery, while gold coins kept for some days in their pockets become blanched. Gold-leaf imparts to transmitted light a blue-green hue.

Alloys of Gold. Pure gold is used only for certain chemical processes, and beaten into leaf for gilding; the Staffordshire potteries consuming for this purpose alone £60,000 worth annually. All other gold, be it used for jewellery or for coinage, is always alloyed with copper or silver to produce the degree of hardness requisite for hammering, stamping, &c. Generally such alloys are considered as consisting of so many carats to the unit, the pound or half-pound being divided into 24 carats, each of which contains 12 grains. What is termed 18 carat gold is a unit of 24 carats of alloy, containing 18 carats gold and 6 of silver or copper. If the latter, the alloy is termed *red;* while if silver is used, it is termed *white;* and if both metals are alloyed with the gold, the caratation is termed *mixed.* In most countries there are legally fixed certain standards for gold jewellery. In this country, 16, 18, and 22 carat gold is stamped, or, as it is termed, *Hall marked;* in France, 18, 20, and 22 carat; in Germany, 8, 14, and 18 carat, and also under the term of *Joujou* gold, a 6 carat gold, used for jewellery, to be electro-gilt. Among the coined gold of European States the term carat is almost everywhere replaced by the expression of so many parts fine per mille. Exceptionally fine gold coins are the Austrian ducats, 23 carats 9 grains, $\frac{986 \cdot 11}{1000}$ of gold; the Dutch, or more correctly Holland, ducats, $\frac{983}{1000}$ or 23 carats 6 to 6·9 grains gold. Neither of these coins are at present a legal tender in Austria or Holland, but they are continually made at the Utrecht Mint, having been for many years the circulating medium in the North Baltic and White Sea ports, as well as in the Black Sea, Levant, and Egypt. Originally they were coins of the Holy Roman Empire (Germany). The English sovereigns and half-sovereigns are coined from $\frac{11}{12}$ or 22 carat gold; or in thousands $= \frac{916}{1000}$; the Prussian Friedrich d'Or $= \frac{903}{1000}$; Wilhelm d'Or $= 21\frac{2}{3}$ carat; the 20-franc pieces of France, Belgium, Switzerland, and Italy $= 21$ carat $7\frac{1}{5}$ grain, or $\frac{900}{1000}$. According to the Vienna Treaty of 1857, the current gold coins of Germany are made in 1000 parts of 900 of gold and 100 of copper, the relative value of silver to gold being taken as 1 : 15·3, or 1 : 15·5.

Colour of Gold. As all gold alloys, commercially or industrially used, exhibit colours different from that of pure gold, it is customary to produce superficially on such alloys the deep yellow of fine metal by boiling in a solution of common salt, saltpetre, and hydrochloric acid; the effect is the evolution of some chlorine, which dissolving a small quantity of the gold, again deposits it as a film of very pure gold. Electro-gilding is, however, frequently substituted for this colouring process.

Testing the Fineness of Gold. Jewellers and goldsmiths generally use touch-needles made from varying gold alloys. The resistance of the streak made upon the touchstone to the action of the dilute nitro-muriatic acid is the test of the fineness of the gold; but it is clear that this method is only approximative, and it cannot be relied on, as jewellery is often superficially coated with a film of pure gold. The most reliable test is afforded by cupellation, for which purpose the gold alloy to be tested is, according to its colour, fused with twice or three times, or an equal weight of silver, and about ten times its weight of lead. This compound alloy is submitted to cupellation in a muffle. The button which remains on the cupel is first flattened on an anvil, next annealed, and rolled into a thin strip, and then boiled with strong nitric acid to dissolve the silver, the remaining gold being washed with boiling water, dried, re-ignited in the muffle, and finally, when cold, weighed.

Applications of Gold. It is not necessary to speak of the well-known uses of gold, the most extensive being its application to coinage, and next that to gilding and jewellery. Gold in sheets $\frac{1}{8}$ inch thick has been used to cover the large dome of Isaac's Church, at St. Petersburg, while three, at least, of the countless crosses on the domes of the Moscow churches are made of solid gold; a portion of one of the domes of a church in the Kremlin is likewise plated with gold.

Gilding. This is done either with gold-leaf, or by means of the cold process, the wet process, fire-gilding, or electro-gilding.

Gilding with Gold-leaf. Gold-leaf, applied in gilding on wood and stone, is prepared in the following manner:—Fine gold is molten and cast into ingots, which are hammered and rolled into thin sheets about an inch in width, technically termed ribbon. The ribbon is cut into small pieces an inch in length, which are placed between pieces of parchment, and beaten out to a moderate thinness. Goldbeaters' skin—the exterior membrane of the *intestina crassa* of oxen—is then substituted for the parchment, and the hammering continued until the metal is of extreme tenuity. The refuse gold of this operation is used for the preparation of bronze-gold for painters. The articles to be gilded with gold-leaf are first painted over with a suitable varnish or size, and the gold-leaves pressed on gently with a piece of soft cotton-wool. Iron and steel, as, for instance, swords, gun-barrels, &c., are first bitten, as it is termed, with nitric acid, next heated to about 300°, and then covered with gold-leaf.

Gilding by the Cold Process. For this purpose fine gold is dissolved in aqua regia; clean linen rags are soaked in this solution, and then burnt to tinder, consisting of carbon and very finely divided gold. This tinder is rubbed on the article to be gilded with a cork moistened in brine; the metallic surface to be gilded should be well polished.

Gilding by the Wet Way. This process is carried out by placing the article to be gilded in either a dilute solution of chloride of gold in ether, which rapidly evaporates, or in a boiling dilute aqueous solution of the same salt, and adding to it carbonate of soda or potassa solution. Iron or steel should be first superficially coated with a film of copper by immersion in a dilute sulphate of copper solution; or these metals, after being bitten with nitric acid, are painted over with a solution of chloride of gold in ether. A solution of chloride of gold in solution of pyrophosphate of soda has lately been suggested as a suitable bath.

Fire-gilding. Articles of bronze, brass, copper, silver, especially buttons and ornaments of military uniforms, are gilt with an amalgam of gold and mercury, 2 parts of the former and 1 of the latter being applied by means of a solution of nitrate of mercury. The articles being next heated in a muffle, the volatile metal escapes, leaving an adhering film of gold, which may either remain dull or be polished, the colour being preserved in the former case by a momentary immersion in a fused mixture of nitre, alum, and common salt, and immediately after in cold water. If it be desired to leave only some portions of the gilding dull, the portions to be afterwards polished are covered with a mixture of chalk, sugar, gum, and sufficient water to form a paste. The *rationale* of the action of the fusing mixture is that chlorine gas is evolved, which, as the term runs, bites the gold. If it is desired to impart a red-gold colour, a paste of wax, bolus, basic acetate of copper, and alum is spread on the gilding, and the article held over a clear fire, the result being the reduction of the copper, which combines with the gold. As the use of the so-called quicksilver-water (nitrate of mercury) is very injurious to the operatives, M. Masselotte, of Paris, coats the articles with mercury, afterwards with gold, and again with mercury, by means of galvanism. Finally, the mercury is volatilised by ignition in a muffle, so arranged that the vapours escape only in the flue. According to M. H. Struve, so-called fire-gilt articles are not really covered with a simple film of gold, but with an amalgam of gold and 13·3 to 16·9 per cent. of mercury. Electro-gilding will be treated in a separate section.

Cassius's Purple. The preparation which bears this name was discovered by Dr. Cassius, at Leyden, in the year 1683. It is prepared by adding to a solution of chloride of gold a certain quantity of sesquichloride of tin. Dr. Bolley prescribes the following process:—First, 10·7 parts of the double chloride of tin and ammonium are digested with pure metallic tin until the metal is quite dissolved, 18 parts of water are then added, and the liquid mixed with the gold solution previously diluted with 36 parts of water. The result is the throwing down of a purple or black-coloured precipitate, about the chemical constitution of which nothing is certainly known. Well-prepared Cassius's purple should contain 39·68 per cent. of gold.

Salts of Gold. The double salts of chloride of gold and sodium ($AuCl_3,NaCl + 2HO$), and the corresponding potassium salt ($2AuCl_3,KCl + 5HO$), are employed in photography and medicine.

MANGANESE AND ITS PREPARATIONS.

Manganese. Of all the ores of manganese met with in various degrees of oxidation, only the peroxide, mineralogically known as pyrolusite, polianite, and technically as glass-makers' soap, is industrially of much importance. When perfectly pure this mineral consists of 63·64 per cent. of manganese, and 36·36 per cent. of oxygen, its formula being MnO_2; but the ore, as met with in commerce, frequently contains baryta, silica, water, and sometimes oxides of iron, nickel, cobalt, and lower oxides of manganese, viz., Braunite, Mn_2O_3; Manganite, Mn_2O_3,H_2O; Hausmannite, Mn_3O_4; and various other minerals, as potassa compounds, lime, &c. In Germany, the ore is purified by most ingeniously contrived machinery, which might be very advantageously applied to a great many other metallic ores and phosphatic minerals. Manganese is industrially employed in making oxygen, the preparation of bromine and iodine, glass-making, colouring enamels, for producing mottled soaps, in puddling iron, and in dyeing and calico-printing, for preparing permanganate of potassa; but the largest consumers are the manufacturers of chlorine. The bulk of the manganese of commerce is derived from Germany, which supplies about 700,000 cwts. to Europe annually. It is found also very largely and of excellent quality in Spain, as well as in Italy, Greece, Turkey, Sweden, and British India.

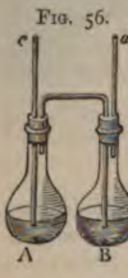
Testing the quality of Manganese. The value of manganese for technical purposes depends—1. On the quantity of oxygen it is capable of yielding, or the quantity of chlorine it will evolve, not taking into account the O of the MnO. 2. On the nature and quantity of the substances soluble in acids, such as the carbonates of lime and baryta, protoxide of iron, which, not yielding chlorine, saturate a certain quantity of hydrochloric acid. But even if these impurities are absent, it may happen that, of two samples of manganese, one requires more acid than the other to evolve the same bulk of chlorine gas, as, for instance, when one of the samples contains in addition to peroxide of manganese (MnO_2) also the sesquioxide (Mn_2O_3), especially if the latter is present as hydrate. 3. On the quantity of water, which may amount even to 15 per cent.

According to the experiments of Dr. Fresenius, the most suitable temperature for drying a weighed sample of manganese, in order to estimate the water it contains, is 120°, no water of hydratation being expelled at that heat; but for commercial analysis the drying of a sample at 100° is quite sufficient, provided it be kept at that heat for some hours consecutively. Among the many methods proposed for testing manganese, that originally invented by Drs. Thompson and Berthier, and improved upon by Drs. Will and Fresenius, is based on the fact that a molecule of peroxide of manganese treated with sulphuric acid is capable of converting, by the O given off, 1 molecule of oxalic acid into 2 molecules of CO_2.

$$\left.\begin{array}{l}\text{1 mol. Peroxide of manganese, } MnO_2\\ \text{1 mol. Sulphuric acid, } H_2SO_4\\ \text{1 mol. Oxalic acid, } C_2H_2O_4\end{array}\right\}\text{ give }\left\{\begin{array}{l}\text{1 mol. of Sulphate of protoxide of manganese, } MnSo_4.\\ \text{2 mols. of Carbonic acid, } 2CO_2.\\ \text{2 mols. of Water, } 2H_2O.\end{array}\right.$$

From the weight of CO_2 evolved is determined the quantity of peroxide of manganese contained in the sample. The operation is performed in the apparatus shown in Fig. 56. The flasks A and B are fitted with perfectly tight-fitting corks, perforated for admitting the glass-tubes, as seen in the woodcut. In the flask A is placed the mixture of previously dried manganese and oxalic acid, with enough water to fill about one-third of the flask. The flask B is about half-filled with strong sulphuric acid; the end of the tube *c* is plugged with a piece of wax and the apparatus weighed. Next some air is sucked out of B, by means of the tube *d*, so as to cause a small quantity of acid to run over into A; thereupon the evolution of CO_2 sets in, and the escaping gas passing through the acid in B is dried. The suction having been repeated, the wax plug at *c*, as soon as the evolution of CO_2 ceases, is for a moment removed, and the suction again repeated to remove all the CO_2 from the apparatus. The plug of wax is now replaced and the apparatus again weighed; the loss of weight gives by calculation the quantity of peroxide of manganese contained in the sample, if one holds in view that 2 molecules CO_2.($CO_2 = 88$) stand to 1 molecule MnO_2 as the quantity of carbonic acid found to x. If 2·98 grms. of dried manganese are taken, and the quantity of CO_2 divided by 3, the centigrammes of CO_2 lost express the proportion per cent. of pure peroxide of manganese contained in the sample; to 1 part of manganese 1¼ parts of neutral oxalate of potassa should be taken for the experiment. If the sample of manganese happens to contain carbonates, it has, previously to being tested, to be treated with very dilute nitric acid, and of course well washed with distilled water and afterwards dried. For other methods of testing manganese, the reader is referred to Mr. Crookes's work on "Select Methods in Chemical Analysis."

FIG. 56.



PERMANGANATE OF POTASSA.

Permanganate of Potassa.

This salt ($KMnO_4$), used for disinfecting, bleaching, and other oxidising purposes, and constantly employed in chemical laboratories, owes its efficiency to the fact that, in contact with dilute sulphuric acid, it yields protoxide of manganese and oxygen ($Mn_2O_7 = 2MnO + 5O$). The permanganate of potassa is for technical purposes prepared in the following manner:—500 kilos. of caustic potassa solution at 45° B. (= 1·44 sp. gr.) are added to 105 kilos. of chlorate of potassa and the mixture evaporated to dryness, there being gradually added 180 kilos. of powdered manganese, and the heating continued to the fusion of the mass, which is stirred until cold. The powder thus obtained is heated in small iron crucibles to a red heat, and when semi-fluid is cooled; the mass is next broken up and put into a large cauldron filled with hot water, and left standing for about an hour. The clear liquid having been decanted from the sediment, hydrated peroxide of manganese, is evaporated to crystallisation; 180 kilos. of manganese yield 98 to 100 kilos. of crystallised permanganate. Approximately the process may be elucidated as follows:—

a. By the fusion of the potassium manganate and chloride of potassium:—

$$6MnO_2 + 2KClO_3 + 12KOH = (3K_2MnO_4) + KCl + 6H_2O;$$

β. During the solution of the fused mass in water, the manganate of potassium is converted into hydrate of potassa, hydrate of peroxide of manganese, and permanganate of potassa:—$3K_2MnO_4 + 6H_2O = 4KOH + 2KMnO_4 + MnO_2 + 4H_2O$. Consequently one-third of the manganic acid is lost by the formation of peroxide of manganese. This also occurs when, according to M. Tessié du Motay's plan, the conversion of manganate of potassa into permanganic acid is effected by sulphate of magnesia:—$3K_2MnO_4 + 2MgSO_4 = 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2MgO$. Dr. Staedeler therefore suggests that the manganate of potassa should be converted into permanganate by chlorine, according to the formula:—$K_2MnO_4 + Cl = KCl + KMnO_4$. For disinfecting purposes a mixed permanganate of potassa and soda, or even the latter alone, is usual; the well-known Condy's fluid is a solution of this salt in water containing per-sulphate, not proto-sulphate of iron. Permanganate of potassa is used to some extent in dyeing, and for staining wood.

ALUMINIUM.

($Al = 27{\cdot}4$; Sp. gr. $= 2{\cdot}5$).

Preparation of Aluminium. Aluminium, discovered at Göttingen, in 1827, by Dr. Wöhler, belongs in the shape of its oxide to the most widely dispersed as well as the most commonly occurring materials on our globe. The properties of this metal were more particularly studied in 1853 by Dr. Deville, who found that aluminium is far less readily acted upon in the molten state by oxygen, in the cold by dilute acids and by boiling water, than was at first thought to be the case, and this eminent author's researches gave rise to the production of this metal for industrial purposes, two manufactories existing in France, viz., at Salyndres and Amfreville, and one in England, at Washington, county Durham.

Aluminium is obtained from the double chloride of aluminium and sodium by the aid of the latter alkali-metal, which is prepared for this and other purposes by the ignition of a mixture of 100 parts of calcined soda, 15 parts of chalk, and 45 parts of small coal. Chloride of aluminium is best prepared from bauxite, native hydrate of alumina, which, having been previously mixed with common salt and coal-tar, is next heated in an iron retort with chlorine gas, the result being the formation of carbonic oxide and the double chloride of aluminium and sodium, which volatilises, and is condensed in a reservoir lined with glazed tiles. The salt so obtained contains iron, and consequently the aluminium derived from it is alloyed with that metal. The double chloride of aluminium and sodium is converted into metallic aluminium by being heated in a reverberatory furnace with sodium; while the aluminium is set free, a slag is formed consisting of the double salt with excess of chloride of sodium. Professor H. Rose, at Berlin, first used cryolite for his experiments on aluminium, the mineral bearing that name being a compound of the double fluorides of aluminium and sodium ($Al_2Fl_3 + 6NaFl$). This mineral being treated at a high temperature with sodium yields aluminium and fluoride of sodium, and the latter treated with quick-lime yields caustic soda and fluoride of calcium.

Properties of Aluminium. The colour of this metal is intermediate to those of zinc and tin; its hardness exceeds that of tin, but is less than that of zinc and copper, and about the same as that of fine silver; it is a very sonorous metal, rather brittle, malleable to some extent, readily rolled into thin sheets, and may be beaten into leaf; on the other hand, it is not ductile. Aluminium does not rust by exposure to air, and it may be even heated to redness without suffering much oxidation. When fused, however—it melts at 700°—it oxidises so much as to necessitate the use of a flux—best chloride of potassium—to absorb the alumina which is formed. It is very readily and rapidly dissolved by hydrochloric acid and solutions of caustic potassa and soda, hydrogen being copiously evolved; but the metal is not in the least acted upon by nitric acid. It does not amalgamate with mercury. With tin it yields an alloy of considerable hardness, yet to some extent malleable; with copper in the proportion of 90 to 95 per cent. of copper and 10 to 5 per cent. of aluminium, it forms aluminium-bronze. This alloy, in colour similar to gold, is used for artificial jewellery and small ornaments. Aluminium does not alloy with lead. The aluminium of commerce is never quite pure, always containing silicium, found by Dr. Rammelsberg even to 10·46 per cent., and frequently present to 0·7 to 3·7 per cent.; while the quantity of iron varies from 1·6 to 7·5 per cent.

Applications. Aluminium is now not so much in use: when first introduced aluminium jewellery was the order of the day. The metal is at present more usefully employed for small weights, light tubes for optical instruments, and to some extent for surgical instruments. The price, however, of this metal, £5 12s. per kilo., is too high to admit of its extended use; while great lightness combined with comparative strength are its only prominent qualities.

MAGNESIUM.

($Mg=24$; Sp. gr. 1·743).

Magnesium. As an oxide, and in combination with chlorine and bromine, as well as with other metalloids, magnesium is found in very large quantities, for instance, in sea-water and carnallite, as sulphate of magnesium, as kieserite, schoenite, kainite, in rocks as a pure carbonate, and as magnesian limestone; further as a silicate in meerschaum. Metallic magnesium has but limited commercial applications. It is silvery white in colour, somewhat affected by the oxygen of the air, but not more so than zinc; fuses at about the same temperature as that metal, and when heated a little above this point, burns with an intensely brilliant white light, and in oxygen gas the combustion is attended with a light almost equal to bright sunlight. Magnesium may be readily drawn into wire; it is at the ordinary temperature of the air as malleable as zinc, and boils and distils over at about the same temperature as that metal. Magnesium is at present only applied to yield an intense light in photography, and for signals; for this latter purpose it was extensively used in the Abyssinian campaign (1868). It has been suggested to alloy magnesium instead of zinc with copper.

Magnesium is prepared by a process very similar to that of aluminium manufacture:—Sodium is ignited with either chloride of magnesium—Bunsen, Deville, and Carron methods—or the double fluoride of magnesium and sodium—Tissier's plan—or the double chloride of magnesium and sodium—Sonstadt's method. Dr. H. Schwarz employs the double chloride of calcium and magnesium, and M. Reichardt carnallite, double chloride of magnesium and potassium. Several other suggestions have been made as to the mode of preparing this metal, but it does not appear that they are available in practice. Magnesium is manufactured on the large scale by the Magnesium Metal Company at Manchester, and the American Magnesium Company at Boston, the English firm producing about 20 cwts. annually.

ELECTRO-METALLURGY.

Application of Galvanism. It is one of the most prominent properties of the continuous electric current, that it is capable of decomposing compound substances in such a manner as to cause the constituents to be deposited on or near the place where the current leaves the body to be decomposed; this property is termed *electrolysis*, the body decomposed being termed *electrolyte*, and the places where the electric current enters and leaves *electrodes*; the positive pole of the battery being named *anode*, and the negative *cathode*. The constituents of the body decomposed by electricity are termed *ions* (from ιων, participle of ειμι, to go); that deposited or separated at the anode (+ pole) being distinguished as the *anion*, and that making its appearance at the cathode the *cation*. An electric current strong enough to decompose a molecule of water is also capable of decomposing a molecule of a binary compound; accordingly the quantities by weight of a body decomposed by the electric current are proportional to the chemical equivalents. **Electrolytic Law.** The main laws of electrolysis were discovered by Faraday, who was the first to show that the constituents attracted by the anode (+ pole) are electro-negative, and those by the cathode

(– pole) electro-positive. As water is a common solvent, it frequently occurs that during electrolysis its elements are secondarily decomposed. For instance, sulphate of copper gives, at the anode oxygen gas, and at the cathode metallic copper, because the oxide of copper appearing at this pole is at once de-oxidised by the simultaneous appearance of hydrogen: the oxygen set free at the positive plate combines with the zinc, forming an oxide, converted by the acid into sulphate of zinc; so that for every equivalent (63·4) of copper deposited, one equivalent (65·2) of zinc is dissolved. If, instead of sulphate of copper, suitable solutions of gold, silver, &c., are employed, the electro-deposition of these metals can be effected.

Electrotyping. The following are the chief technical applications of electrolysis:—Electrotyping. It has just been said that the copper separated electrolytically from the sulphate of that metal is deposited in a coherent state, and if the operation is continued for some time the layer of metal may become sufficiently thick to admit of being detached from the form upon which it was deposited. This principle of electrotyping was discovered in 1839, simultaneously at St. Petersburg by Dr. Jacobi, and at Liverpool by Mr. Spencer; among those who have laboured to improve this art, are Messrs. Becquerel, Elsner, Smee, Ruolz, Elkington, and many others. The metallic solution applied for the preparation of casts to be electrotyped is always a saturated solution of sulphate of copper, and the form, technically termed the pattern or matrix, upon which it is desired to deposit the copper, should not consist of any metal, such as zinc, tin, or iron, acted upon by a solution of sulphate of copper. The matrix is usually, if it be a metal, made of copper; but more frequently it consists of gypsum or gutta-percha. In order to render the electric current uniform, the zinc plate of the battery is amalgamated by dipping it in hydrochloric or dilute sulphuric acid, and then rubbing mercury over the surface with a brush or piece of soft rag.

Reproduction of Copper-Plate Engravings. The engraved copper-plate to be reproduced is placed at the bottom of a wooden trough lined with resin or ashphalte. Above the plate is fixed a wooden frame, on which is strained a sheet of bladder or parchment, to serve as a diaphragm; and on the top of the frame a plate of zinc is placed, and connected with the copper-plate by a strip of lead. A saturated solution of sulphate of copper is poured into the bottom of the trough, and in order to maintain the saturation a few crystals are added. Above the porous diaphragm a concentrated solution of sulphate of zinc is placed. This plan is also pursued in electrotyping woodcuts, stereotype-plates, &c.

Deposition of Metals. To reproduce medals and other small objects a weak current only is required. The plate or object on which it is desired to cause the deposition to take place is suspended vertically from the cathode, and a plate of the metal to be deposited from the anode; in proportion as the metal is precipitated at the cathode, it is dissolved at the anode, leaving the concentration of the fluid unchanged. Such substances as are non-conductors, wax, paraffine, and gypsum, are first superficially coated with some conducting material, as graphite, silver, or gold-bronze. Gutta-percha is an excellent material for casts, owing to its becoming plastic in boiling water. According to M. von Kobell, a tough malleable copper is obtained by adding to the copper solution some sulphate of soda and sulphate of zinc. Unless a rather weak current is applied, the copper is separated from its solution in a spongy state; on no account should the current be strong enough to decompose water.

Electro-Plating with Gold and Silver. In order to apply a coating of gold or silver to copper, brass, bronze, or other metallic alloy, the surface should be first very thoroughly cleaned by boiling in a caustic soda solution. Smee's battery—a platinised silver plate, and a plate of amalgamated zinc—is now generally used, the elements being placed in leaden vessels lined with asphalte. The solution of gold or silver in cyanide of potassium is employed as the decomposition liquid, in which the objects to be silvered or gilded are suspended by a wire connected with the negative pole of the battery;

and to another wire, connected to the positive pole of the battery, is fastened a piece of platinum, which is also immersed in the liquid of the decomposition-cell. The whole process only lasts a few minutes, the cathode during the time being moved backwards and forwards by hand to render the deposit uniform. Plates of gold or silver are generally used instead of platinum at the anode, and become gradually dissolved by, and maintain, the cyanide solution at a constant strength.

Gold Solution. 100 grms. of cyanide of potassium are dissolved in 1 litre of distilled water, and 7 grms. of very fine gold in nitro-hydrochloric acid, this solution being evaporated to dryness on a water-bath, the residue dissolved in distilled water, and to the solution some cyanide of potassium added; or the gold salt obtained on evaporation may be dissolved in distilled water, and the solution carefully precipitated with sulphate of iron, the finely-divided gold being collected on a filter, next washed with distilled water, and finally dissolved in cyanide of potassium.

Silver Solution. This solution is prepared by dissolving well-washed chloride of silver in the above solution of cyanide of potassium, so as to obtain a saturated solution of cyanide of silver, afterwards to be diluted with an equal bulk of water.

Copper, bronze, brass, iron, and steel can be electro-plated directly; but polished steel, tin, and zinc have to be first coated with a film of copper. German or nickel-silver is now generally electro-plated. The thickness of the film of silver may vary from 1-42nd to 1-450th, or even to 1-9400th of a millimetre, corresponding to 1·240 grms. of silver on 1 square metre of surface. Frequently the best electro-plated ware made in this country is afterwards coated with a very thin film of palladium to prevent the silver being affected by sulphuretted fumes.

Copper Solution. For the purpose of electro-coppering, a solution of oxide of copper in cyanide of potassium is the most suitable fluid; this solution is prepared by first decomposing a solution of sulphate of copper in water, with the aid of caustic potassa and grape sugar, so as to obtain a precipitate of sub-oxide (red oxide) of copper, which, having been collected on a filter, and well washed, is next dissolved in a solution of cyanide of potassium. For the purpose of electro-coppering iron and steel, M. Weil, of Paris, prepares a fluid—350 grms. of cupric sulphate, 1500 grms. of potassio-tartrate of soda (*sal seignette*), and 400 to 500 grms. of caustic soda dissolved in 10 litres of water.

M. Oudry's method of depositing copper on iron candelabras, gas lamps, fountain ornaments, &c., is in some particulars quite different, the copper not being immediately deposited on the iron, which is first coated with an impermeable layer of a kind of red-lead paint, graphite being afterwards rubbed in for the purpose of rendering the surface of the object a conductor. To obtain a coating of copper 1 millim. in thickness, such articles as candelabra are left in the solution for 4½ days; the ornamental fountains of the Place la Concorde, Paris, have been for a period of two months in the solution.

Zinc and Tin Solution. To coat iron with zinc, a solution of the sulphate of the latter metal may be used, but the so-called galvanised iron of commerce is made by a different process, viz., by placing the iron to be coated in a bath of molten zinc, covered, for the purpose of preventing oxidation, with a layer of molten tallow or paraffin. For the purpose of electro-tinning, a solution of tin in caustic soda is employed, the anode being of tin.

A so-called electro-steeling, really a deposit of iron on the copper plates used for engraving, is effected by M. Meidinger in the following manner:—The bath is a solution of sulphate of iron and chloride of ammonium: to the copper pole of the battery a plate of iron, and to the zinc pole the engraved copper plate, are connected. These steeled plates serve for as many as 5000 to 15,000 impressions. This method has been applied to stereotyping with great success, and indeed the deposition of iron electrolytically is a valuable addition to technology.

Etching by Galvanism. This process is based upon the fact that, under certain conditions, the substances separated at, combine with the electrodes, the consequence being that the electrode is gradually corroded and destroyed. The copper-plate intended to be etched is uniformly covered with a mixture of 4 parts of wax, 4 of asphalte, and 1 of black pitch; the design is then drawn or rather scratched with proper tools through this non-conducting layer, and the plate attached to the anode of a galvanic battery, and placed in a solution of sulphate of copper, containing also a copper-plate connected to the negative electrode of the battery. On this plate is deposited the copper of the solution, while the oxygen of the decomposed water, with the sulphuric acid, act upon the portions of metal not covered with the protective layer and produce the etching.

Metallochromy, Or galvanic painting, consists in depositing thin films of oxide of lead in a coherent state on metal plates, thus producing Nobili's colours. The oxide of lead is, for this purpose, best dissolved in caustic potassa or soda solutions. In England, this method of ornamenting is not much applied; but at Nuremburg, where toys are largely manufactured, this process is very simply carried out by placing the metallic object, previously connected with the cathode of a battery, in a concentrated solution of oxide of lead in caustic potassa, while to the anode is affixed a piece of platinum foil.

Electro-Stereotyping. For the purpose of reproducing printing-types by galvanic means, a wax impression of the type is placed in the deposition-cell. This operation is also employed for the reproduction of woodcuts, gutta-percha being used as a mould.

Glyphography. By this name is understood a process for reproducing woodcuts, but it is now altogether obsolete, having been superseded by electro-typing. A further disadvantage was, that the glyphographic plates could not be printed from the same matrix as type.

Galvanography. At the suggestion of Dr. von Kobell, the reproduction of some kinds of drawings and pictures has been tried, in order to enable exact copies to be printed from plates electrolytically obtained from the original drawings; but this method, of very difficult and costly execution, is superseded by photography.

DIVISION II.

CRUDE MATERIALS AND PRODUCTS OF CHEMICAL INDUSTRY.

CARBONATE OF POTASSA.

($K_2CO_3 = 138{\cdot}2$; in 100 parts, 68·2 potassa and 31·8 parts carbonic acid.)

Sources whence Potassa is derived.

The substance known in chemistry as carbonate of potassa is generally termed *potash*, because it was formerly obtained from wood-ash, which, after lixiviation with water, was evaporated to dryness in cast-iron pots. Potassa occurs native in considerable quantities, but never free, being combined with silica in many minerals, also in combination as chloride of potassium, sulphate of potassa, and in various plants with organic acids. The following are the sources whence potassa is industrially obtained:—

A. Inorganic sources of Potasssa.
- I. The salt minerals of Stassfurt and Kalucz; products—carnallite, sylvin, kainite, and schoenite.
- II. Feldspar and similar minerals.
- III. Sea-water and the mother-liquor of salt-works.
- IV. Native saltpetre.

B. Organic sources of Potassa.
- V. The ashes of several plants.
- VI. The residue of the molasses of beet-root sugar after distillation.
- VII. Sea-weeds, as a by-product of the manufacture of iodine.
- VIII. The suint of the crude wool of sheep.

Potassa Salts from the Stassfurt Salt Minerals.

I. The very abundant salt-rocks near Stassfurt, in Prussia, and Kalucz, in Hungary, chiefly yield carnallite, sylvin (ClK), and kainate, a compound of sulphate of potassa and magnesia with chloride of magnesium. Carnallite, so named in honour of Carnall, a Prussian mining engineer, consists, in 100 parts, leaving the bromine out of the question, of—

Chloride of potassium	27
Chloride of magnesium	34
Water..	39
	100

Formula—KCL, $Mg\left\{\begin{matrix}Cl_2\\Br_2\end{matrix}\right. + 6H_2O$. This salt is applied in the manufacture of—

- α. Chloride of potassium.
- β. Sulphate of potassa.
- γ. Potash (carbonate).

a. **Preparation of Chloride of Potassium.**—According to the process originally patented (1861) by Mr. A. Frank, the abraum salts are ignited in a reverberatory furnace, with or without the aid of a current of steam, and next lixiviated with water, the resulting liquor yielding chloride of potassium. The *rationale* of this process is:—1. That the carnallite of the abraum salts is separated by the action of the water into chloride of potassium and chloride of magnesium. 2. The latter salt, on being ignited in a current of steam, is decomposed into hydrochloric acid, which escapes, and magnesia, which is practically insoluble in water, and which consequently remains. This process is not found to answer well on the large scale, because the abraum salts contain other chlorides, the chloride of sodium and tachydrite, by the presence of which the decomposition of the carnallite is hindered. Dr. Grüneberg, therefore, suggested that the abraum salts should be first mechanically purified, that is to say, the different components of the abraum salts should be separated from each other according to their varying specific gravity, which for—

Carnallite is = 1·618
Chloride of sodium is = 2·200
Kieserite is = 2·517

The abraum salt having been ground to a coarse powder is passed through sieves, and treated as minerals are in metallurgical processes, with the difference that, instead of water, which of course would dissolve the salts, a thoroughly concentrated solution of chloride of magnesium is applied, this solution not acting upon the salts, and being, moreover, obtained as a by-product in enormously large quantities. The above-mentioned salts settle in layers according to their densities, the carnallite forming the upper, and the kieserite the lowest layer. The carnallite is at once applied to the preparation of chloride of potassium; the middle layer of common salt is so free from other foreign salts as to be fit for domestic use; the kieserite, after having been washed with cold water to remove any adhering chloride of sodium, is applied to the manufacture of sulphate of potassa, to be presently described. However, the greater number of manufacturers at Stassfurt prefer another plan, applying the five following operations to the abraum salts as delivered from the salt quarries:—1. Lixiviation of the carnallite with a limited quantity of hot water, sufficient to dissolve the chlorides of potassium and magnesium, leaving the bulk of the common salt and magnesian sulphate. 2. Crystallising the chloride of potassium by artificially

Fig. 57.

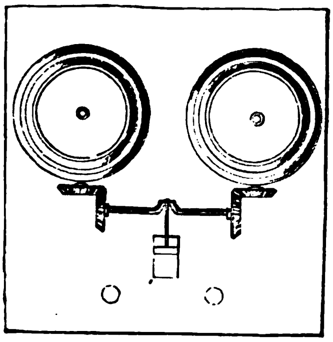
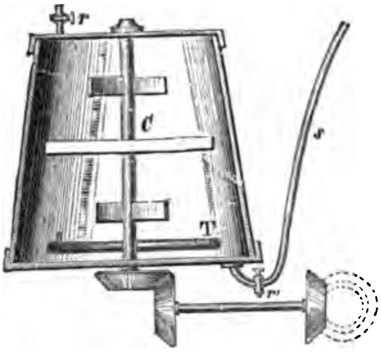


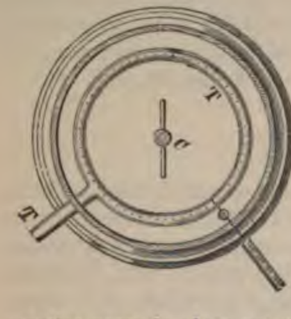
Fig. 58.



freezing. 3. Evaporating and cooling the mother-liquor to produce a second yield of crystallised chloride of potassium. 4. Again evaporating and cooling the mother-liquor, which yields the double salt of the chlorides of potassium and magnesium, or artificial carnallite, which is next treated in the same manner as the native salt. 5. Washing, drying, and packing the chloride of potassium.

1. The carnallite is put into cast-iron lixiviation vessels and mixed with three-fourths of its weight of water, previously employed for the washing of crude chloride of potassium, and, therefore, containing a large quantity of common salt and some chloride of potassium; steam, at 120°, and at a pressure of 30 lbs. to the square inch, is forced through the perforated circularly bent tube, T (Fig. 59) at the bottom of the vessel. In Mr. Douglas's works the lixiviation vessels, Figs. 57, 58, and 59, have a cubical capacity of 20 tons. They are closed with a tightly-fitting lid, an opening being cut for the escape of surplus steam. The stirrer, C, is kept in motion by steam-power. When the admission of steam and the stirring has been continued about three hours, the contents of the vessels are left at rest for two days, after which the saturated solution has a density of 32° B. = 1·286 sp. gr., and is forced by steam pressure into crystallising vessels; the residue in the lixiviation vessels, amounting to about one-third of the weight of the carnallite, is again treated as described.

FIG. 59.



2. The crystallisation vessels are of wood or sheet-iron, 1·20 metres diameter, by 1·5 to 1·9 metres height. The chloride of potassium crystallises in combination with common salt, and is strongly impregnated with the very soluble and highly deliquescent chloride of magnesium; the salt deposited at the sides of the vessel contains upwards of 70 per cent. of chloride of potassium, while that collected at the bottom contains only 55 per cent. If shallow vessels are employed, the saline solution cools more rapidly, and a finer grained salt is obtained, mixed, however, with impurities, and requiring more washings, an operation which, with the coarse salt, has only to be performed once to yield 80 per cent. chloride of potassium. Most of the chloride of potassium sold by the manufacturers contains 80, and in some cases 85 and 90, per cent. of the pure salt.

3. The evaporation of the first mother-liquor is carried on in iron pans of various sizes. As by the evaporation common salt is largely deposited, which has a tendency to cake at the bottom of the pans, and check the conduction of heat, the pans are set so as to receive the action of the flame only on the sides (Fig. 61), and the liquid kept constantly

FIG. 60.

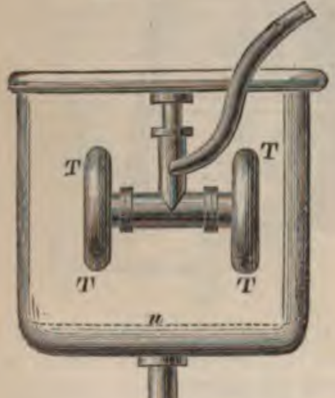
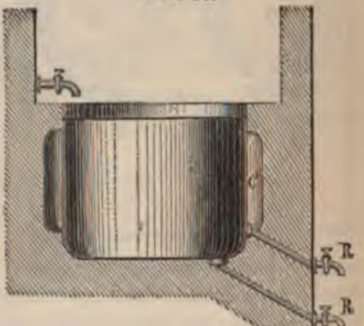


FIG. 61.



stirred. When the liquor has been reduced to about two-thirds of its bulk, with a density of 33° B. = 1·298 sp. gr., it is run into the crystallising vessels. The mass remaining in the evaporating pan, consisting of 60 to 65 per cent. common salt, 6 per cent. chloride of potassium, and 30 per cent. double sulphates of magnesium and potassium, is used as manure. Steam-heated evaporating pans, represented in Fig. 60, are employed by some manufacturers; the four steam-tubes, T, are placed parallel to the sides of the vessel, and open in *u*, the waste steam being carried off by the tube T′. As might be expected, the concentration of the liquor is more rapidly performed by means of steam, but the crystallisation of the second crop of salt is poorer, yielding only 50 to 60 per cent. chloride of potassium, and requiring two to three washings to accumulate 80 per cent. pure potassium salt.

4 and 5. The second mother-liquor is again concentrated by evaporation to 35° B. = sp. gr. 1·299, yielding a saline mass similar to the residue of the first evaporation, and to which it is added and used as a manure. On being submitted to crystallisation, this last liquor yields artificial carnallite, treated as the salt obtained from the native deposit, giving, however, with less labour 80 to 90 per cent. chloride of potassium. The chloride of potassium, after washing with pure water, is dried either in rooms heated by steam, or in a moderately-heated reverberatory furnace. The dry salt is then packed in casks, each containing about 500 kilos.

β. The preparation of sulphate of potassa may be effected:—

a. From chloride of potassium and sulphuric acid.

b. By Longmaid's (see Soda Manufacture) roasting process, viz., the calcination of chloride of potassium and sulphuret of iron, and in metallurgical processes where chloride of potassium is used instead of chloride of sodium.

c. From chloride of potassium and kieserite.

d. From kainite.

The conversion of chloride of potassium into the sulphate of potassa by double decomposition with sulphate of soda is not practicable on the large scale, as the two salts have a tendency to form double salts; therefore, the methods *a* and *b* are practically available only under certain peculiar conditions. A small quantity of chloride of potassium, obtained in Scotland as a by-product of the preparation of kelp, is converted into sulphate of potassa by the means in use for the manufacture of soda (*quod vide*). The leading points in the manufacture of sulphate of potassa by the aid of the sulphuric acid contained in kieserite are the following:—First schoenite and carnallite are prepared by dissolving chloride of potassium and kieserite in boiling water, and crystallising the solution thus obtained:—

$$\left.\begin{array}{l}\text{4 mols. Kieserite}\\ \text{3 mols. Chloride of potassium}\end{array}\right\} = \left\{\begin{array}{l}\text{2 mols. Schoenite.}\\ \text{1 mol. Carnallite.}\end{array}\right.$$

The schoenite and artificial carnallite are separated by crystallisation, and the former decomposed by chloride of potassium:—

$$\left.\begin{array}{l}\text{4 mols. Schoenite}\\ \text{3 mols. Chloride of potassium}\end{array}\right\} = \left\{\begin{array}{l}\text{4 mols. of Sulphate of potassa.}\\ \text{2 mols. of Schoenite.}\\ \text{1 mol. of Carnallite.}\end{array}\right.$$

The sulphate of potassa crystallises first, and is simply purified by washing with water. As kainite is found in very large quantities among the saline deposits near Stassfurt, it is also used for the preparation of sulphate of potassa; by a simple washing with water, the chloride of magnesium contained in the kainite is removed, and the salt thus converted into schoenite:—

$$\left.\begin{array}{l}\text{Kainite}\\ \text{—Chloride of magnesium}\end{array}\right\} = \text{Schoenite.}$$

The schoenite is then employed in the manufacture of sulphate of potassa by being treated with chloride of potassium; the sulphate of potassa thus obtained is used either in alum or potassa manufacture, or as a potassa manure.

γ. Preparation of Carbonate of Potassa or Mineral Potash.—Very many suggestions have been made for converting by simple means chloride of potassium and sulphate of potassa into carbonate of potassa, industrially known as potash; but most of the plans proposed are unfit for use on the large scale, and even the method adopted by Leblanc for soda manufacture has not been in every case successful when applied to the production of chloride of potassium. At Kalk, on the opposite bank of the Rhine to Cologne, a process, said to be based upon Leblanc's method, is successfully in operation, but the real arrangements are carefully kept secret, no one being allowed to visit the works; however, it is stated that sulphate of potassa containing schoenite is mixed with chalk and small coals, and calcined, the calcined mass being lixiviated when cool, and yielding carbonate of potassa in solution, and a residue of sulphide of calcium.

Mode of Obtaining Potassa from Feldspar.

II. Potassa-salts from feldspar. It has been found by the analysis of minerals entering largely into the constitution of rocks, that potassa is present in considerable quantities. The following may be taken as instances:—Orthoclase, or potash feldspar, contains from 10 to 16 per cent.; potash mica, 8 to 10 per cent.; trachyte, glaukonite, phonolithe, 7 to 8 per cent.; porphyry, granulite, and mica schist, 6 to 7 per cent.; granite, syenite, gneiss, 5 to 6 per cent.; dolerite, basalt, kaolin, and clay, 1 to 2 per cent.

Before the discovery of the potassa-salt deposits at Stassfurt, Kalucz, and elsewhere, there were many suggestions made as to the obtaining of the potassa on the large scale; but at present this branch of industry lies dormant, notwithstanding the theoretical value of Mr. Ward's (1857) suggestion that feldspar should be mixed with fluor-spar, both finely pulverised—the fluorine being equal in quantity to the potassa contained in the fluor-spar—a mixture of chalk and hydrate of lime added, the mass ignited in kilns or gas-retorts, and finally treated with water to yield caustic potassa and a residue, which, after another calcination, yields excellent hydraulic lime.

Potassa-Salts from Sea-Water.

III. Dr. Usiglio found that the water of the Mediterranean contains in 10,000 parts by weight 5·05 parts of potassa; and after the removal of the more readily crystallisable salts left by the spontaneous evaporation of the water by the sun's heat, this natural mother-liquor is applied to the preparation of potassa-salts, according to the following method:—

The process now in use near Aigues Mortes, and other localities in proximity to the Mediterranean, was invented by Professor Balard, the discoverer of bromine, and yields from 1 cub. met. of mother-liquor, equal to about 75 cub. mets. of sea-water, at 28° B. = 1·226 sp. gr. 40 kilos. of sulphate of soda, 120 kilos. of refined common salt, and 10 kilos. of chloride of potassium. It has been found, however, that this method is rather costly, and the mother-liquor is generally left to spontaneous evaporation, yielding the three following kinds of salt:—*a.* The first salt separated from a liquor of 32° B. = 1·266 sp. gr., only impure common salt. *b.* The second salt separated from a liquor, 32° to 35° B. = 1.266 to 1·299 sp. gr., consisting of equal parts of common salt and Epsom-salt, and termed mixed salt. *c.* The third salt, 35° and 37° B. = 1·299 to 1·321 sp. gr., termed summersalt. The second salt having been dissolved in fresh cold water, the solution is placed in Carré's ice-making machine, and yields sulphate of soda by an exchange of its constituents. The third salt is dissolved in boiling water, yielding on cooling half its potassa as kainite. The mother-liquor, containing carnallite, common salt, and bitter, or Epsom-salt, yields sulphate of soda, and, when treated with chloride of magnesium, all its potassa as carnallite, which, by being washed with water, yields chloride of potassium. In this way it has become possible to obtain 45 per cent. of the potassa of the mother-liquor as chloride of potassium, and 55 per cent. of schoenite, which is converted into sulphate of potassa.

Potash from the Ashes of Plants.

IV. The residue left from the ignition of the organic matter, or wood, as it is usually termed, of plants, contains those mineral substances which the plant has taken from the soil, chiefly potassa, soda, lime, magnesia, small quantities of the protoxides of iron and manganese, combined with phosphoric, sulphuric, silicic, and carbonic acids, and also with the haloids. These combinations are not, however, the same as those existing in the living plant, because the high temperature of the ignition has the effect of changing the affinities. Plants growing near the sea generally contain large quantities of soda, while those inland contain generally more potassa. The quantity of ash varies not only for different kinds of plants, but for various parts of the same plant, very succulent plants and the most succulent parts generally yield the largest quantity of ash; herbs yield more ash than shrubs, shrubs more than trees, and the leaves and bark of these more than the wood. It is evident that the inorganic matter, chiefly alkaline salts, being contained in the juice of plants in a soluble state, the quantity must of necessity be greatest in the juicy and succulent parts.

Dr. Böttger found the ash of beech-wood to contain—

21·27 per cent. of soluble salts,
78·73 „ „ of insoluble salts.

The soluble salts were found to be—

Carbonate of potassa	15·40 per cent.
Sulphate of potassa	2·27 „ „
Carbonate of soda	3·40 „ „
Chloride of sodium	0·20 „ „
	21·27 per cent.

The value of an ash for the manufacture of potash is chiefly dependent, in the first place, upon the quantity of potassic carbonate it will yield, upon the abundance of the wood or other vegetable product, and the cost of labour. The undermentioned woods yield, on an average, for 1000 parts, the following quantities of potash:—

Pine	0·45	Beech-bark	6·00
Poplar	0·75	Dried ferns	6·26
Beech	1·45	Stems of maize (Indian corn)	17·50
Oak	1·53	Bean-straw	20·00
Box-wood	2·26	Sunflower-stems	20·00
Willow	2·85	Nettles	25·03
Elm	3·90	Vetch-straw	27·50
Wheat-straw	3·90	Thistles	35·37
Bark from oak-knots	4·20	Dried wheat-plant previous to blooming	47·00
Cotton-grass (*Eriophorum vaginatum*)	5·00	Wormwood	73·00
Rushes	5·08	Fumitory	79·00
Vine-wood	5·50		
Barley-straw	5·80		

According to M. Höss, 1000 parts of the following kinds of wood yield—

	Ash.	Potash.		Ash.	Potash.
Pine	3·40	0·45	Willow	28·0	2·85
Beech	5·80	1·27	Vine	34·0	5·50
Ash	12·20	0·74	Dried ferns	36·4	4·25
Oak	13·50	1·50	Wormwood	97·4	73·00
Elm	25·50	3·90	Fumitory	219·0	79·90

The preparation of potash from vegetable matter is effected in three operations, viz.:—

a. The lixiviation of the ash.
b. The boiling down of the crude liquor.
c. The calcination of the crude potash.

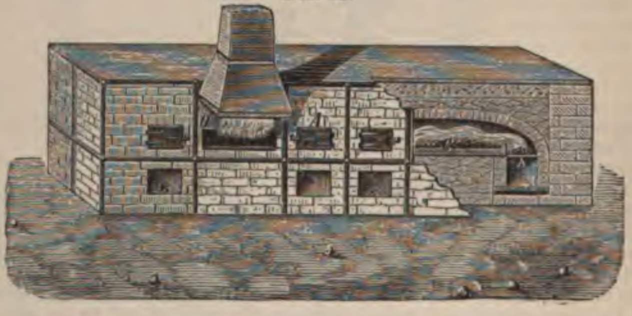
The combustion of the vegetable matter should be so conducted as to prevent its becoming too violent, and giving rise to the combustion of some of the reduced potassa-salt; nor should too strong a current of air be admitted for fear of the ash being mechanically carried off. A distinction is made abroad—no potash from wood or other vegetable matter being produced in the United kingdom, nor wood used as fuel in sufficient quantities to yield ash for the preparation of potash—between the ash obtained by the combustion of the refuse wood of forests and the ash from wood used as fuel, the former being termed *forest-* and the latter *fuel*-ash. As ash from other fuel than wood may be mixed with fuel-ash, a sample may be roughly tested by lixiviation, and the density of the liquor taken by the areometer, the higher the specific gravity the larger the quantity of soluble salts. Formerly the forest ash was purposely prepared, and sold to potash-boilers. There is still known in Eastern Prussia and Sweden a material termed *okras* or *ochras*, holding a position intermediate to crude ash and potash.

a. The lixiviation of the ash effects the separation of the soluble from the insoluble saline matter, the former amounting to about 25 to 30 per cent. of the entire weight of the ash. The operation is carried on in wooden vessels shaped like an inverted truncated cone, and provided with a perforated false bottom, which is covered with straw; in the real bottom a tap is fixed for removing the liquor. If the lixiviation is systematically carried on several of these vessels are placed together, forming what is termed a battery, and under each a tank to receive the liquor. The ash to be lixiviated is first separated from the coarse particles of charcoal, next put into a small square water-tight wooden box, and thoroughly saturated with water for at least twenty-four hours. By this proceeding the lixiviation is greatly assisted, and the silicate of potassa to some extent decomposed by the action of the carbonic acid of the atmosphere. The next step is to transfer the wet ash to the lixiviation vessel, care being taken to press it tightly down on to the false bottom; cold water is then poured in, until the liquor begins to run off at the taps left open for that purpose. The liquor which runs off, after the water has remained some little time in contact with the ash, is found to contain about 30 per cent. of soluble salts, afterwards decreasing to about 10 per cent., when hot water is employed to complete the lixiviation. The insoluble residue left in the lixiviation-tub is of value as a manure, on account of the phosphate of lime it contains, and is also used in making green bottle-glass, and for building up saltpetre-beds.

b. Boiling down the liquor. The liquor obtained by lixiviation is of a brown colour, owing to organic matter, humin or ulmine, which the carbonate of potassa has dissolved from the small chips of imperfectly burnt charcoal. The evaporation is carried on in large shallow iron pans, fresh liquor being from time to time added, and the operation continued until a sample of the hot concentrated liquor exhibits on cooling a crystalline solid mass. When this point is reached the fire is gradually extinguished, and as soon as the contents of the pan are sufficiently cold to handle, the solid salt mass is broken up; its colour is a deep brown. This crude product, containing about 6 per cent. of water, is known in the trade as crude, or lump-potash. It is evident that this method of boiling down may cause considerable damage to the iron pans, therefore in many instances the operation is conducted in a somewhat different manner. The liquid is kept stirred with iron rakes, and the salt, instead of forming a hard solid mass, is obtained as a granular powder, containing upwards of 12 per cent. water. Some manufacturers first separate the sulphate of potash, which, being less soluble, crystallises before the carbonate, a deliquescent salt, is separated from the liquor; in most cases, however, this operation is only carried on where the sulphate of potash is required for alum-making. The pearl-ash or potash of commerce almost invariably contains a large quantity of sulphate of potash.

c. In order to expel all the water and to destroy the organic matter, the saline mass is calcined, and as this operation was formerly performed in cast-iron pots, the salt has obtained the name of potash. A calcining furnace, Fig. 62, is now used, distinguished from ordinary reverberatory furnaces by being provided with a double fire-place. These hearths, one of which is exhibited in section at A, FIG. 62, are placed at right angles to each other, and the flame and smoke meeting in the centre of the furnace, pass off at *o*, the work-hole, into the chimney, K. Wood is used as fuel, and as the heating of the furnaces requires a very large quantity, they are only in use when a sufficient supply of crude potash is ready for being operated upon. The furnace is thoroughly heated in about five to six hours, care being taken to fire gradually, and to bring the interior of the furnace to nearly red heat, so that the vapour due to the combustion of the wood may not condense inside the furnace, but be carried off by the flue. The crude potash, broken up to egg-size lumps, is next placed in such quantities at a time as may suit the size of the calcining hearth; for instance, if the hearth is roomed to contain 3 cwts., that quantity is divided into three portions and put in at intervals of a few minutes. The first effect of the heat is to expel the water from the potash, the escape of the steam being promoted by stirring

FIG. 62.



the mass with iron rakes. In about an hour all the water is driven off, and the mass takes fire in consequence of the burning of the organic matter, the salt at first being blackened, but gradually becoming white as the carbon burns off. As soon as this stage is reached, the potash is removed to the cooling-hearth, and when cold, packed in well-made wooden-casks, which, as this salt is very hygroscopic, are rendered as air-tight as possible. The heat of the furnace has to be well regulated to prevent the potash becoming semi-fused, in which case it would attack the siliceous matter of the fire-bricks; the workmen from time to time take a small sample to test how far the calcination is complete.

We, in Europe, obtain a considerable quantity of potash from the United States and Canada, known as American potash, of which there are three different kinds, viz.:— 1. Potash prepared as described. 2. Pearl-ash, or potash, purified by lixiviation, decantation from sediment, boiling down, and the calcination of the salt thus obtained. 3. Stone-ash, a mixture of uncalcined potash (potassic carbonate), and caustic potash obtained by treating the crude potash liquor with caustic lime, and boiling down the mass to dryness; this article has the appearance of the crude caustic soda of this country, but is usually coloured red by oxide of iron; the lumps, stone-hard, are from 6 to 10 centims. in thickness, and contain upwards of 50 per cent. caustic potash. The under-mentioned analyses exhibit the varying composition of the potash of commerce:—Sample 1 is from Kasan (Russia); analyst, M. Hermann. 2. Tuscany. 3 and 4—the latter of a reddish colour—from North America. 5. Russia. 6. Vosges (France); analyst of 2, 3, 4, 5, and 6, M. Pesier. 7. Helmstedt, in Brunswick; analyst, M. Limpricht. 8. Russia; analyst, M. Bastelaer.

	1.	2.	3.	4.	5.	6.	7.	8.
Carbonate of potash ..	78·0	74·1	71·4	68·0	69·9	38·6	49·0	50·84
Carbonate of soda ..	—	3·0	2·3	5·8	3·1	4·2	—	12·14
Sulphate of potash ..	17·0	13·5	14·4	15·3	14·1	38·8	40·5	17·44
Chloride of potassium..	3·0	0·9	3·6	8·1	2·1	9·1	10·0	5·80
Water	—	7·2	4·5	—	8·8	5·3	—	10·18
Insoluble residue	0·2	0·1	2·7	2·3	2·3	3·8	—	3·60

The calcined potash varies in colour, being either white, pearl-grey, or tinged with yellow, red, or blue. The red colour is due to oxide of iron, the blue to the manganates of potash, a hard, light porous, non-crystalline mass, never entirely soluble in water. Formerly, a large quantity of potash was obtained from the residues of wine-making, and called vinasse, the semi-liquid left after the alcohol has been distilled from the wine, and containing, among other substances, argol, or crude bitartrate of potash; it was boiled down, and next calcined, yielding a kilo. of very good potash for every hectolitre of vinasse. The large quantity of potash thus formerly produced may be judged from the fact that 19 of the wine-producing departments of France, those only where large quantities of wine are converted into alcohol, technically termed *trois six* and *cinq huit*, yield annually about 9 to 10 million hectolitres of vinasse, at the present time employed for the preparation on the large scale of cream of tartar, glycerine, and tartaric acid.

Potash from Molasses. V. Of late years, the manufacture of potash salts from the vinasse left after the distillation of fermented beet-root molasses has been added as a new branch of industry by M. Dubrunfaut, and introduced into Germany by M. Varnhagen, in the year 1840, at Mucrena, Prussian Saxony.

Beet-root, on being subjected to ignition, yields an ash containing a large percentage of potash, a fact first observed in the early part of this century by M. Mathieu de Dombasle, a celebrated French agriculturist, who discovered that 100 kilos. of dried beet-root leaves yield 10·5 kilos. of ash, containing 5·1 kilos of potash; but this author's idea that the leaves might be cut off and gathered for the purpose of potash manufacture, proved erroneous, in so far that the growth of the roots was greatly impeded. After the publication of M. Dubrunfaut's researches on this subject, in 1838, the vinasse of the beet-root molasses distillation was evaporated to dryness, next calcined, and the calcined mass refined for the production of potash and other salts of that base, an industry which has obtained a great development, as may be judged from the fact that the quantity of these materials produced on the European continent in 1865 amounted to 240,000 cwts.

The reader who desires details on this subject is referred to the work, "On the Manufacture of Beet-Root Sugar in England and Ireland," by Wm. Crookes, F.R.S., &c., p. 25c *et seq.*

The molasses from beet-root sugar consists, previous to the fermentation and distillation, of the undermentioned substances, as recorded by the several analysts whose names are subjoined:—

	Brunner.	Fricke.	Lunge.	Heidenpriern.	
Water	15·2	18·0	18·5	19·0	19·7
Sugar	49·0	48·0	50·7	46·9	49·8
Salts and organic substances	35·8	34·0	30·8	34·1	30·5

The following analyses by M. Heidenpriern exhibit the average composition of the ashes of molasses:—

	1.	2.	3.
Potassa	51·72	47·67	50·38
Soda	8·00	11·43	8·29
Lime	5·04	3·60	3·12
Magnesia	0·18	0·10	0·18
Carbonic acid	28·90	27·94	28·70

The remainder of the 100 parts consists of phosphoric and silicic acids, chlorine, oxide of iron, &c. The quantity of ash amounts to 10 or 12 per cent. According to Dubrunfaut the alkalimetrical degree of the ash of beet-root sugar molasses is a constant, as the ash obtained from 100 grms. of molasses neutralises on an average 7 grms. of sulphuric acid (H_2SO_4).

The molasses is generally treated in the following manner:—It is first diluted with either water or vinasse to 8° or 11° B=1·056 or 1·078 sp. gr., and mixed with 0·5 to 1·5 per cent. of a pure mineral acid, the object of this addition being not simply the neutralisation of the alkali, but also the conversion of dextrine and such unfermentable sugar into fermentable sugar. Formerly, sulphuric acid was used, but upon the recommendation of M. Wurtz, hydrochloric acid is now generally employed, the advantage being the formation of readily soluble chlorides, instead of comparative insoluble alkaline sulphurets, the action of the organic matter present in the molasses.

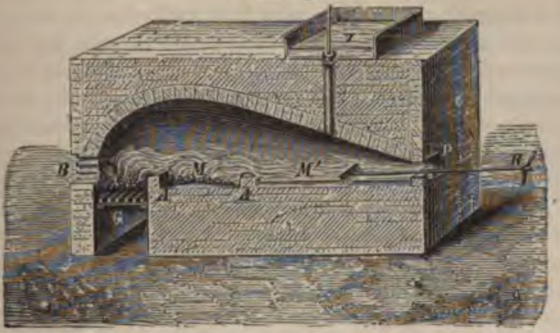
The diluted molasses is next mixed with yeast, left to ferment, and the alcohol distilled off; the residue is a liquid of about 4° B. density [=1·027 sp. gr.] containing undecomposed yeast, ammoniacal salts, various organic substances, and all the inorganic salts of the beet-root juice. The potassa is present in this liquid as nitrate chiefly, although by the addition of hydrochloric acid a portion of this salt is decomposed, red nitrous fumes sometimes being seen in the fermentation room. Evrard suggests that the saltpetre should be separated from the beet-root molasses by evaporation, and further purified by the aid of the centrifugal machine. The acidity of the vinasse is neutralised by chalk, and afterwards it is evaporated to dryness in an iron vessel, the total length of which is 20·3 metres, by an average width of 1·6 metre, extended at the top to 2 metres, the depth being 0·34 metre. The vessel is made of stout boiler plate, strengthened by stays and angle irons, and is divided into two divisions, the larger of which has a length of 14·3 metres, and is the real evaporating pan, while the other is used as a calcining furnace, and covered with an arch of fire-bricks 0·6 metre high. The fire-place is 1·3 metre wide, and the fire-box has a surface of 3·3 square metres. The evaporation is effected by surface heating, that is to say, the flame and hot gases from the burning fuel, after passing across the fire-bridge are conducted over the surface of the vinasse, the calcining pan being nearest to the fire, while the evaporating pan is at its other extremity in contact with the flue or chimney. The vinasse, having been run off from the still, is kept in cisterns, from which it is forced by means of a pump into a reservoir so placed as to admit of the liquid running in a constant stream into the evaporating pan. At a first operation both the evaporating and the calcining pan are filled with vinasse, but afterwards the latter is filled regularly with concentrated thick liquor, which is simply carbonised, the organic matter being only destroyed.

The daily average of carbonised vinasse is about 5 to 5½ cwts. The composition of that substance may be gleaned from the following approximate analysis:—

Insoluble matter	= 23	per cent
Sulphate of potassa	= 11·07	,,
Chloride of potassium	= 11·61	,,
Carbonate of potassa	= 31·40	,,
Carbonate of soda	= 23·26	,,
Silicic acid and hyposulphite of potassa	= traces	,,
	99·34	,,

In Germany, the calcined vinasse is generally sold to saltpetre manufacturers, but in Belgium and France this material is calcined, lixiviated, and the salts it contains separately obtained. For this purpose the vinasse is first evaporated to 38° or 40° B. (1·33 to 1·35 sp. gr.), and next carbonised and calcined in a furnace constructed as exhibited in Fig. 63. V is a reservoir containing the concentrated vinasse, which by means of a tube is gradually run into the furnace, of which G is the fire-place, M the calcination space, destined to contain the concentrated or carbonised vinasse, which is evaporated to dryness and calcined in M′; a door is fitted to each compartment, and at P, the end of the furnace opposite to the fire-place. The air required for the calcination is admitted partly through the ash-pit, partly through the openings, B, in the brickwork. The thickish liquid vinasse admitted into M′ is constantly stirred, and, as soon as it is quite dry, it is shovelled across the brickwork ridge, A′, into the calcining space, M, care being taken to again fill M′ with concentrated vinasse. The organic matter of the saline mass soon takes fire, emitting noxious fumes. The calcination is greatly aided by the access of air at B, and also to some extent by the nitrate of potassa present. The temperature has to be regulated to prevent the salts becoming fused and forming a hard compact mass, in which case the sulphate of potassa would be reduced to sulphuret of potassium, a salt which

FIG. 63.



could not be removed. The calcined vinasse, technically termed *salin*, contains, when removed from the furnace, 10 to 25 per cent. of insoluble substances, viz., carbonate and phosphate of lime, more or less charcoal, and in addition 3 to 4 per cent. moisture; the remainder consists of carbonates of potash and soda, sulphate of potassa, chloride of potassium, and sometimes cyanide of potassium in considerable quantity. The relative quantities of potassa and soda are, of course, not at all constant, but vary according to the soil on which the beets have grown; it has been observed in France that the molasses obtained from beets grown in the Département du Nord are less rich in potassa than those grown in the Départements de l'Oise et de la Somme. The average composition of the salin is:—

7 to 12 per cent. of sulphate of potassa.
18 to 20 ,, of carbonate of soda.
17 to 22 ,, of chloride of potassium.
30 to 35 ,, of carbonate of potassa.

The complete composition of the salin may be gathered from the following tabulated results:—

	a.	*b.*	*c.*	*d.*
Water and insoluble matter.. ..	26·22	19·82	17·47	13·36
Sulphate of potassa	12·95	9·88	2·55	3·22
Chloride of potassium	15·87	20·59	18·45	16·62
Chloride of rubidium	0·13	0·15	0·18	0·21
Carbonate of soda	25·52	19·66	19·22	16·54
Carbonate of potassa	23·40	29·90	42·13	50·05
	100·00	100·00	100·00	100·00

The method of separating the soluble salts from each other, invented by M. Kuhlmann, is generally executed as follows:—The saline mass is first broken up and granulated by the aid of grooved iron rollers, after which it is placed in lixiviation-tanks, each containing 26·4 cwts., and arranged precisely in the same manner as those in use in soda works. The liquor tapped from the tanks has a sp. gr. of 1·229 (= 27° B.); the insoluble residue is used as manure. The liquor having been collected in a large reservoir, capable of containing some 210 hectolitres, is concentrated by waste heat (*abgängiger wärme*) to a density of 1·26 (= 30° B.); on cooling, the greater part of the sulphate of potassa crystallises, and is removed, care being taken to wash off the adhering mother-liquor. The sulphate thus obtained contains 80 per cent. pure potassic sulphate, the rest being carbonate of potassa and organic matter: this material is converted into potash by Leblanc's process. The liquor at 30° B. is next poured into evaporating-pans, each capable of containing 90 hectolitres, and concentrated by means of heat and a steam pressure of 3 atmospheres (= 45 lbs. to the square inch) to a density of 42° B. (= 1·408). By this operation a mixture of carbonate of soda and sulphate of potassa is separated, which frequently exhibits 30 alkalimetrical degrees; the liquor is transferred from the evaporating-pans to crystallising vessels, in which it is cooled down to not less than 30°. If, by carelessness, the temperature should fall below 30°, the chloride of potassium crystals become mixed with a layer of carbonate of soda. The liquor at a temperature of 30°, and having a density of 42° B., is again transferred to evaporating-pans, each capable of containing 20 hectolitres, and evaporated

In winter to a sp. gr. of 1·494 (= 48° B.), and
In summer to a sp. gr. of 1·51 (= 49° B.)

By this operation sodic carbonate separates, the first and purer portions of which are of 82 alkalimetrical degrees, and the last of 50° only. After the separation of the salt, the remaining liquor is poured into small crystallising vessels, each capable of holding 2½ hectolitres, and having been left standing for some time, yields in each vessel about 130 kilos. of a crystalline salt, mainly composed according to the formula $(K_2CO_3 + Na_2CO_3 + 12H_2O)$. The remaining mother-liquor, when evaporated to dryness and calcined, yields a semi-refined potash, tinged with red by oxide of iron. This product is again lixiviated with water, and the liquor having been concentrated to 1·51 to 1·525 sp. gr. (= 49° to 50° B.), deposits a large quantity of sulphate of potassa and carbonate of soda. The mother-liquor having been again evaporated and calcined, yields a potash consisting in 100 parts of—

Carbonate of potassa	91·5
Carbonate of soda	5·5
Chloride of potassium and sulphate of potassa	3·0
	100·0

The carbonate of soda possessing a strength of 80 to 85 alkalimetrical degrees is refined by being washed with a very concentrated aqueous solution of sodic carbonate, and thus brought to a strength of fully 90 alkalimetrical degrees.

The sulphate of potassa, chloride of potassium, and the double salt of the two carbonates, are purified and re-crystallised. The following analyses exhibit the composition of refined potash obtained from beet-root sugar molasses:—

	a.	*b.*	*c.*
Carbonate of potassa	88·73	94·39	89·3
Carbonate of soda	6·44	traces	5·6
Sulphate of potassa..	2·27	0·28	2·2
Chloride of potassium	1·00	2·40	1·5
Iodide of potassium	0·02	0·11	—
Water	1·39	1·76	—
Insoluble substances	0·12	—	—

a and *b* are from Waghäusel in Baden; *c* is doubly refined French potash. The crude potash from beet-root sugar works, a product not to be confused with *salin*, is composed as follows:—

	a.	*b.*	*c.*	*d.*	*e.*
Carbonate of potassa ..	53·9	79·0	76·0	43·0	32·9
Carbonate of soda ..	23·1	14·3	16·3	17·0	18·5
Sulphate of potassa ..	2·9	3·9	1·19	4·7	14·0
Chloride of potassium..	19·6	2·8	4·16	18·0	16·0

a is French product; *b*, from Valenciennes; *c*, from Paris; *d*, Belgian; *e*, from Magdeburg, Prussia.

Potassa Salts from Sea-weeds. VI. Potassa salts are obtained in large quantities from various sea-weeds, as a by-product of the manufacture of bromine and iodine. The three following methods are employed for this purpose:—

a. The old calcination method, consisting in a complete reduction of the weeds to ash, and the methodical lixiviation of that product, so as to obtain various salts by crystallisation.

b. The carbonisation, or Stanford's method, consisting in the dry distillation of the weeds to convert them into a carbonaceous mass, afterwards lixiviated, while products are simultaneously obtained, the sale of which considerably lessens the cost of the preparation of the potassa salts.

c. A third mode of treatment, that of Kemp and Wallace, consisting in boiling the weeds with water, evaporating the solution, and carefully incinerating the residue.

The oldest method is still the most generally employed in France, on the coasts of Brittany and Lower Normandy, especially in the neighbourhood of Brest and Cherbourg, and in Scotland and Ireland.

The process is mainly conducted as follows:—After drying in the air, the plants are incinerated, the result of which is the formation of a black semi-fused mass, which in France is termed *Varech* or *Vraic*, and in England and Scotland is known as *kelp*. A distinction is made between the kelp obtained by the incineration of the weeds, *Fucus serratus* and *Fucus nodosus*, found on rocks near the sea coast, and the kelp obtained from the plant botanically known as *Laminaria digitata*, thrown upon the coast during the storms. The latter is richer in potassa salts, but contains much less iodine; it is found plentifully on the western coast of Scotland and Ireland, while on the eastern coast of the British Isles the other weed is the chief source of kelp, having an average composition of:—

Insoluble matters	57·000
Sulphate of soda	10·203
Chloride of potassium	13·476
Chloride of sodium	16·018
Iodine	0·600
Other salts	2·703
	100·000

The best kelp met with in commerce is that from the island of Rathlin, the value at Glasgow amounting to £7 10s. to £10 10s. per ton of 22½ cwts.; while Galway kelp is valued at only £2 or £3 per ton, owing to the large quantity of salt it contains. 22 tons of moist sea-weed yield:—

Medium kelp	1 ton.
Chloride of potassium	5 to 6 cwts.
Sulphate of potassa	3 cwts.

The Scotch mode of treating kelp is briefly the following:—The material is first broken into small lumps, and put in large iron cauldrons, hot water being added to exhaust all the soluble matter. This operation follows the method of the manufacture of soda from common salt, to be presently considered. The water is first made to act upon nearly exhausted kelp, and at last with quite fresh kelp, until a liquid is produced marking 36° to 40° Twaddle = 1·18 to 1·20 sp. gr. The insoluble residue contains chiefly silica, sand, carbonate of lime, carbonate of magnesia, its sulphates and phosphates, and particles of charcoal, and is used for bottle-glass manufacture. The liquor from the kelp is evaporated in large cast-iron semi-globular cauldrons by the direct action of a coal fire, and contains chiefly chloride of potassium, a comparatively small quantity of chloride of sodium, sulphate and carbonate of potassa, carbonate of soda, some iodide of potassium, sulphuret of potassium, and dithionite of potassium and sodium. The mode of separating these salts from each other is based upon their varying solubility in water, and is therefore conducted by alternate evaporation and cooling. As the sulphate of potassa is the least soluble, it falls to the bottom of the cauldron during the first evaporation, and is collected by the workmen by means of perforated ladles, and brought into the trade as *plate sulphate.* After this salt has been collected the liquid is run into coolers, in which the greater bulk of the chloride of potassium crystallises; the mother-liquor from these crystals is again transferred to the evaporator, and by the continued application of heat, and consequent concentration of the liquid, the common salt is separated. It should be borne in mind that common salt is scarcely more soluble in hot than in cold water, while the solubility of most other salts is greatly increased by a higher temperature; it is therefore possible to push the evaporation and concentration to the point of incipient precipitation of the chloride of potassium, the common salt being then ladled out of the cauldron, and the liquid again run into the coolers in order to obtain another deposit of chloride of potassium, always more or less contaminated with common salt. This operation is repeated four times; the first crop of chloride of potassium contains from 86 to 90 per cent. of this salt, the remainder is chiefly sulphate of potassa; the second and third crop yield a very pure salt, 96 to 98 per cent. of chloride of potassium; the fourth crop contains some sulphate of soda mixed with the chloride of potassium. The liquor left after the fourth crystallisation having a sp. gr. = 1·33 to 1·38 = 66° to 76° Twad., and containing among other compounds sulphate of soda, sulphurets and hyposulphites of the alkalies, alkaline carbonates, and iodide of potassium, is not submitted to further evaporation, but having been poured into shallow vessels placed in the open air is mixed with dilute sulphuric acid, sulphuretted hydrogen and carbonic acid gases being largely evolved, while in consequence of the decomposition of the polysulphurets and hyposulphites, a thick foam of pure sulphur appears on the surface of the liquid. This sulphur is ladled off, and after having been washed on filters and dried, is sold. Almost as soon as the evolution of gas ceases, there is added to the liquid more sulphuric acid and some manganese, and the mixture treated for the preparation of iodine (*quod vide*). In order to guard against loss of valuable substances by volatilisation during the crude and imperfect mode of incineration, it has been tried to simply carbonise the weeds (Stanford's method). The weeds are first dried and strongly pressed into the shape of peat blocks; these are submitted to dry distillation in retorts arranged similarly to those in gas-works. The products of the dry distillation collected in the usual manner contain in 100 parts of fresh weed:—

68·5 to 72·5	parts of	Ammoniacal liquor,
4·0	,,	Tar,
7·0 to 7·5	,,	Carbonised weed, or coke-weed,
2·0 to 2·5	,,	Illuminating gas.

The coke contains 33 per cent. carbon, the remainder consisting of alkaline and earthy salts; the volatile products of the distillation are treated for paraffin, photogen, acetic acid, and ammoniacal salts, the gas being used for lighting purposes. Although Mr. Stanford's mode of treatment is undoubtedly rational, there are difficulties in its practical execution which have prevented its adoption in Scotland as well as in France. The quantity of potash salts obtained from seaweeds in the year 1865 amounted, according to M. Joulin, to a total of 2,700,000 kilos., of which the United Kingdom produced 1,200,000 kilos., the remainder being produced by France.

Since the production of chloride of potassium at Stassfurt and Kalucz has become so extensive, the production of potassa salts from sea-weeds is of little consequence.

Potassa Salts from Suint. VII. The fact is well known that sheep while browsing abstract a considerable amount of potassa, which, after having passed into the blood and tissues, is sweated through the skin, and deposited on the wool as suint. Professor Chevreul's researches have proved that suint constitutes nearly the third part of the weight of crude merino wool, while the soluble portion of the suint consists of the potassa salts of a fatty acid, potassic sudorate (*suintate de potasse*). According to Messrs. Reich and Ulbricht, the fatty acids of suint are compounds of oleic, stearic, and probably palmitinic acids. The better wool contains more suint than the coarser kinds; on an average the quantity of suint amounts to 15 per cent of the weight of the fleece.

Since the year 1860, and based upon the researches of MM. Mauméne and Rogelet, the manufacture of potash salts from the wash-water of the crude wool has become, in the centres of the French woollen manufacture (Rheims, Elbœuf, Fourmies) an industrial branch. The wash-water is valued according to its degree of concentration; 1000 kilos. of wool yielding a liquid which, according to M. Chandelon, has a sp. gr. of 1·03, is paid for at the rate of 5 francs 48 cents.; at a sp. gr. of 1·05, at the rate of 10 francs 45 cents.; sp. gr. 1·25, 18 francs 47 cents. The liquid is evaporated to dryness, the carbonaceous residue put into gas retorts, and heated to redness, the result being the formation of carburetted hydrogen gas and ammonia, which having been eliminated, the gas is used for illuminating purposes. The coke left in the retorts is lixiviated with water to obtain the soluble salts, chloride of potassium, carbonate and sulphate of potassa, which are separated from each other by methods already described.

The residue left after the lixiviation with water contains earthy matter mixed with charcoal so very finely divided that it can be used as black paint. According to MM. Maumené and Rogelet, a fleece weighing 4 kilos. contains 600 grms. of suint, capable of yielding 198 grms. of pure carbonate of potassa; according to M. Fuchs, however, the quantity of suint only amounts to 300 grms., containing—

Sulphate of potassa	7·5 grms.	=	2·5 per cent.
Carbonate of potassa	133·5 ,,	=	44·5 ,, ,,
Chloride of potassium	9·0 ,,	=	3·0 ,, ,,
Organic matter	150·0 ,,	=	50·0 ,, ,,
	300·0 ,,	=	100.0

It appears that the woollen industry of Rheims, Elbœuf, and Fourmies consumes annually 27 million kilos. of wool, the produce of 6,750,000 sheep. According to MM. Maumené and Rogelet this quantity of wool will yield 1,167,750 kilos. of potash, representing a money value of £80,000 to £90,000. According to M. P. Havrez, at Verviers, Belgium, suint is more advantageously worked up for the manufacture of carbonate of potassa and yellow prussiate of potassa than for carbonate of potassa alone. Suint has been recently (1869) chemically investigated by MM. Märker and Schulze (see Journ. für Prakt. Chemie, vol. 103, pp. 193—208). It is clear that the production of potash from the wash-water of sheep's wool can only be carried out in the centres of woollen industry; the sheep-farmers will always do better to return the wash-water and potash compounds it contains to the soil from which the animals have taken it. In an industrial point of view the extensive importation of foreign wool, especially from Australia and the Cape, is of great importance. In 1868 there were imported into the United Kingdom from those countries 63 million kilos. of wool, containing one-third of its weight of suint, from which between 7 and 8 kilos. pure potash could have been obtained, representing a money value of about £260,000.

Preparation of Purified Potash.—The potash formerly obtained by the lixiviation of wood-ash was mainly a mixture of carbonate, sulphate of potassa, and chloride of potassium, the value of each of these salts being of course very different. At the present time, in consequence of the production of pure carbonate of potassa from vinasse, it has become necessary to treat the crude liquor obtained by the lixiviation of wood-ash methodically, so as to obtain the salts separately in as pure a state as possible.

The carbonate of potassa used in chemical and pharmaceutical laboratories was formerly obtained by the ignition of cream of tartar or a mixture of that salt with nitre, as well as by the ignition of acetate of potassa; at the present time it is prepared by the careful ignition of nitrate of potassa with an excess of charcoal, or by the ignition of bi-carbonate of potassa. In England carbonate of potassa is manufactured on the large scale, the pure salt being used in the manufacture of flint-glass, this glass owing its great superiority and perfect want of colour to the application of very pure materials in its manufacture. The preparation is pure crystallised carbonate of potassa, containing from 16 to 18 per cent. water, equal to somewhat less than 2 molecules, the second molecule being partly expelled by the heat applied in the manufacture. This salt is met with in the trade in small cubical crystals; the raw material used in its preparation is American pearl-ash, which, after having been mixed with sawdust for the purpose of converting the caustic alkali and sulphuret of potassium into carbonate of potassa, is ignited and fused in a reverberatory furnace, constructed like those used in the manufacture of soda. When cold the fused mass is treated with water, and the clear liquor having been decanted from the sediment, is evaporated to dryness in a reverberatory furnace; the greyish-black mass thus obtained is again lixiviated with water, and the operation repeated. The white saline mass from the third ignition is again dissolved in water, and gently evaporated until the sulphate of potassa crystallises out; the mother-liquor left is next evaporated until a sample yields on cooling a salt of the composition mentioned above. If this salt is further ignited all the water is expelled, and a dry white granular mass left. The specific gravity of carbonate of potassa solutions at 150 is, according to Dr. Gerlach—

Percentage.	Sp. gr	Percentage.	Sp. gr.
1	1·009	30·000	1·3010
2	1·018	35·000	1·3580
4	1·036	40·000	1·4180
5	1·045	45·000	1·4800
10	1·092	50·000	1·5440
15	1·141	51·000	1·5570
20	1·192	52·000	1·5704
25	1·245	52·024	1·5707

Caustic Potassa. Preparation of Caustic Potassa.—Caustic potassa, hydroxide of potassium, KHO, consists in 100 parts of 83·97 of potassa or dry oxide of potassium, and 16·03 of water. Caustic potassa is prepared on the large scale in England.

The raw material for this preparation is always a crude carbonate of potassa obtained from chloride of potassium, carnallite from Stassfurt, vinasse, or any other source. The crude carbonate is lixiviated with water, and the liquor rendered caustic with quick-lime. A more advantageous method of preparing caustic potassa is to mix sulphate of potassa with limestone and small coal, in sufficiently large quantities, and to ignite this mixture in a furnace. The crude material is, after cooling, lixiviated with water at 500, yielding at once raw caustic potassa liquor, which does not require any further addition of lime. The liquor is put into a steam-boiler and evaporated to a sp. gr. = 1·25; it is next evaporated to dryness in open pans, the foreign salts which separate being removed. Caustic potassa is employed for the conversion of soda-saltpetre into potassa-saltpetre, and with caustic soda for the manufacture of oxalic acid from sawdust. The following reactions, yielding caustic potassa, deserve a brief notice:—1. Decomposition of sulphate of potassa by means of caustic baryta. 2. Conversion of chloride of potassium into silico-fluoride of potassium, and decomposition of that salt by means of caustic lime. 3. Ignition of potassic nitrate with thin sheet-copper. The following table exhibits the quantity of potassa contained in solutions of that substance of varying specific gravity:—

Sp. gr.	Degrees Baumé.	Percentage of potassa.
1·06	9	4·7
1·11	15	9·5
1·15	19	13·0
1·19	24	16·2
1·23	28	19·5
1·28	32	23·4
1·39	41	32·4
1·52	50	42·9
1·60	53	46·7
1·68	57	51·2

SALTPETRE, NITRATE OF POTASSA.

(KNO_3 = 101·2. In 100 parts, 46·5 parts potassa, and 53·5 parts nitric acid.)

Saltpetre. This salt is to some extent a native as well as a chemical product. The well-known flocculent substance often observable on walls, especially those of stables, is composed in a great measure of nitrates; a similar phenomenon is seen in subterranean excavations, and even in many localities the surface of the soil is covered with an efflorescent saline deposit, consisting largely of nitrate of potassa. These deposits are most common in Spain, Hungary, Egypt, Hindostan, on the banks of the Ganges, in Ceylon, and in some parts of South America, as at Tacunga in the State of Ecuador; while in Chili and Peru nitrate of soda, so-called Chili saltpetre, is found in very large quantities under a layer of clay, the deposit extending over a tract of land some 150 miles in length.

Occurrence of Native Saltpetre. Although native saltpetre is met with under a variety of conditions, they all agree in this particular, that the salt is formed under the influence of organic matter. As already stated, the salt covers the soil, forming an efflorescence, which increases in abundance, and which if removed has its place supplied in a short time. In this manner saltpetre, or nitre as it is sometimes called, is obtained from the slimy mud deposited by the inundations of the Ganges, and in Spain from the lixiviation of the soil, which can be afterwards devoted to the raising of corn, or arranged in saltpetre beds for the regular production of the salt. The chief and main condition of the formation of saltpetre, which succeeds equally in open fields exposed to strong sunlight, under the shade of trees in forests, or in caverns, is the presence of organic matter, viz., Humus, inducing the nitre formation by its slow combustion; the collateral conditions are dry air, little or no rain, and the presence in the soil of a weathered crystalline rock containing feldspar, the potassa of which favours the formation of the nitrate of that base. All the known localities where the formation of nitre takes place naturally, including the soil of Tacunga, formed by the weathering of trachyte and tufstone, are provided with feldspar. The nitric acid is due to the slow combustion of nitrogenous organic matter present in the humus, it having been proved that the nitric acid constantly formed in the air in enormously large quantities by the action of electricity and ozone, as evidenced by the investigations of MM. Boussingault, Millon, Zabelin, Schönbein, Froehde, Böttger, and Meissner, has nothing whatever to do with the formation of nitre in the soil, a fact also supported by Dr. Goppelsröder's discovery of the presence of a small quantity of nitrous acid in native saltpetres.

Mode of obtaining Saltpetre. The mode of obtaining saltpetre in the countries where it is naturally formed is very simple, consisting in a process of lixiviation with water, to which frequently some potash is added for the purpose of decomposing the nitrate of lime occurring among the salts of the soil, the solution being evaporated to crystallisation. Soils yielding saltpetre are termed Gay earth or Gay saltpetre. The process by which nitrate of potassa is naturally formed is imitated in the artificial heaps known as saltpetre plantations, formerly far more general than at the present time, it having been found that the importation of Indian saltpetre, and the manufacture of nitrate of potassa by conversion from nitrate of soda, are cheaper sources. Thus, saltpetre beds are to be met with only under peculiar conditions, as, for instance, in Sweden, where all landed proprietors are required to pay a portion of their taxes in saltpetre.

The mode of making these plantations may be briefly described as follows:—Materials containing much carbonate of lime—for instance, marl, old building rubbish, ashes, road scrapings, stable refuse, or mud from canals—is mixed with nitrogenous animal matter, all kinds of refuse, and frequently with such vegetable substances as naturally contain nitrate of potassa, such as the leaves and stems of the potato, the leaves of the beet, sunflower plants, nettles, &c. These materials are arranged in heaps of a pyramidal shape to a height of 2 to 2½ metres, care being taken to make the bottom impervious to water by a well puddled layer of clay, the heap being in all directions exposed to the action of the atmosphere, the circulation of which is promoted through the heap by layers of straw. The heap is protected from rain by a roof, and at least once a week watered with lant (stale urine). The formation of saltpetre of course requires a considerable length of time, but, when taught by experience, the workmen suppose a heap *ripe*, the watering is discontinued, the salt containing saltpetre soon after efflorescing over the surface of the heap to 6 to 10 centims. in thickness; this layer is scraped off, and the operation repeated from time to time until the heap becomes decayed and has to be entirely removed. In Switzerland saltpetre is artificially made by many of the farmers, simply by causing the urine of the cattle, while in stable in the winter time, to be absorbed by a a calcareous soil purposely placed under the loose flooring of the stables, which are chiefly built on the slope of the mountains, so that only the door is level with the earth outside, the rest of the building hanging over the slope, and being supported by stout wooden poles; thus a space is obtained, which, freely admitting air, is filled with marl or other suitable material. After two or three years this material is removed, lixiviated with water, mixed with caustic lime and wood ash, and boiled down. The liquor having been sufficiently evaporated, is decanted from the sediment and left for crystallisation; the quantity of saltpetre varying from 50 to 200 lbs. for each stable.

Treatment of the Ripe Saltpetre Earth. The crude salt from the heaps is converted into potassic nitrate by the following processes:—*a*. The earth is lixiviated with water, this operation being known as the preparation of raw lye. *b*. The raw lye is broken, that is to say, it is mixed with a solution of a potash salt in order to convert the nitrates of magnesia and lime present into nitrate of potassa. *c*. Evaporation of this liquor to obtain crude crystallised saltpetre. *d*. Refining the crude saltpetre.

Preparation of Raw Lye. The ripe earth is lixiviated to obtain all the valuable soluble matter, it being expedient to use as little water as possible in order to save fuel in the subsequent evaporation, for which the liquor is ready when it contains from 12 to 13 per cent. of soluble salts.

Breaking up the Raw Lye. The raw lye, sometimes known as soil water, contains the nitrates of lime, magnesia, potassa, soda, the chlorides of calcium, magnesium, and potassium; also ammoniacal salts and organic matter of vegetable as well as of animal origin. In order to convert the nitrates of lime and magnesia into nitrate of potassa, the raw lye is broken up as it is termed, that is to say, there is added to it a solution of 1 part potassic carbonate in 2 parts water:—

$$\left.\begin{array}{l}\text{Nitrate of lime, } Ca(NO_3)_2\\ \text{Nitrate of magnesia, } Mg(NO_3)_2\\ \text{Carbonate of potassa, } {}_2K_2CO_3\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Nitrate of potassa, } 4KNO_3.\\ \text{Carbonate of lime, } CaCO_3.\\ \text{Carbonate of magnesia, } MgCO_3.\end{array}\right.$$

The chlorides of calcium and magnesium are also decomposed, being converted into carbonates, while chloride of potassium is formed. The addition of the solution of potassa to the raw lye is continued as long as a precipitate is formed; in order, however, to have some approximative idea of the quantity of carbonate of potash which may be required, a test experiment is made with $\frac{1}{2}$ litre of the raw lye.

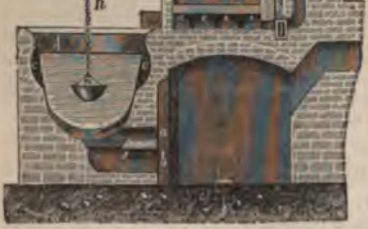
Sometimes sulphate of potassa is used instead of the carbonate, but in that case the magnesia salts of the raw lye have first to be decomposed by milk of lime, an operation which has to be followed by the evaporation of the fluid. If, after this, sulphate of potassa is added, sulphate of lime is precipitated—

$$[Ca(NO_3)_2+K_2SO4=2KNO_3+CaSO4].$$

When chloride of potassium is used for the decomposition of raw lye, the salts of magnesia are first removed by the addition of milk of lime; and the clear supernatant fluid having been decanted from the sediment, there is added a mixture of equal molecules of chloride of potassium and sulphate of soda, the result being the formation of gypsum, while the sodic nitrate generated exchanges with the chloride of potassium, carrying over to the latter the nitric acid, and taking up the chlorine to form common salt.

Boiling down the Raw Lye. The clarified raw lye decanted from the precipitate of the earthy carbonates consists of a solution in which there are present the chlorides of potassium and sodium, nitrate of potassa, carbonate of ammonia, excess of potassic carbonate, and colouring matter. The boiling down of this liquid is effected in copper cauldrons, Fig. 64, so set in the furnace as to admit of the circulation of the hot air and smoke from the fire-place, passing by *c c* below the heating pan, and thence by *g* into the chimney. In some works this waste heat is utilised in drying the saltpetre flour. As the bulk of the fluid in the cauldron decreases by evaporation, fresh lye enters by means of a pipe and tap from the pan, D. About the third day the alkaline chlorides begin to be deposited, and the workmen have then to take great care to prevent these salts from becoming what is technically

FIG. 64.



termed burnt, which might give rise to serious explosions, and for this purpose the liquid is stirred with stout wooden poles. After each stirring the loose saline matter is removed from the boiling liquid by means of perforated copper ladles. However, as a hard deposit is always formed, a peculiar arrangement exhibited in Fig. 64, consisting of a shallow vessel, *m*, suspended by a chain, *k*, and weighted with a piece of stone, is lowered into the middle of the cauldron to about 6 centims. from the bottom, the object being to catch the solid particles, which would, when aggregating, form an incrustation, previously to their reaching the bottom of the vessel; and as no ebullition takes place at *m*, the particles once deposited remain there, and can be readily removed by raising the dish out of the cauldron, and emptying it into a box placed over the cauldron, the bottom of the box being perforated to admit of any liquor which may have been raised with the solid salt to return again to the cauldron. The deposit thus removed consists chiefly of gypsum and carbonate of lime.

When a portion of the impurities contained in the boiling liquid have been removed, the raw lye still frequently contains some chloride of sodium, as this salt is not, as is the case with nitre, more soluble in boiling than in cold water. The abundant crystallisation of the saltpetre is a sign that the lye has been sufficiently evaporated; in order, however, to prove this, a small sample is taken, and if on cooling the nitre crystallises so that the greater part of the sample becomes a solid mass, the liquid is run into tanks and left for 5 or 6 hours, during which time impurities are deposited, and the liquid rendered quite clear. As soon as the temperature of the liquid has fallen to 60°, it is poured into copper crystallisation vessels; after a lapse of 24 hours the crystallisation is complete, and the mother-liquor being separated from the salt is employed in a subsequent operation.

Refining the Crude Saltpetre.

The crude saltpetre is yellow-coloured, and contains on an average some 20 per cent. of impurities, consisting of deliquescent chlorides, earthy salts, and water. The object to be attained by the refining is the removal of these substances. At the present day a large portion of the refined saltpetre met with in commerce is obtained by the refining of the crude saltpetre imported from India. It may be noted that this importation is steadily increasing, there being, in 1860, 16,460,300 kilos., and in 1868, 33,062,000 kilos. of the salt brought to England; and, indeed, the production of saltpetre from natural sources in Europe is now limited to very few and unimportant localities.

The method of refining saltpetre is based upon the fact that nitrate of potassa is far more soluble in hot water than are the chlorides of sodium and potassium. 600 litres of water are poured into a large cauldron, and 24 cwts. of the crude saltpetre are added at a gradually increasing temperature; as soon as the solution boils, 36 cwts. more crude saltpetre are added. Supposing the crude nitre to contain 20 per cent. of alkaline chlorides, the whole of the nitre will be dissolved in this quantity of water, while a portion of the chlorides will remain undissolved even at the boiling-point. The non-dissolved salt is removed by a perforated ladle, and the scum rising to the surface of the boiling liquid by the aid of a flat strainer. The organic matter present in the solution is removed by the aid of a solution of glue—from 20 to 50 grms. of glue dissolved in 2 litres of water are taken for each hundredweight of saltpetre. In order that the saltpetre may crystallise, the quantity of water is increased to 1000 litres, and as soon as this water is added the organic matter entangled in the glue rises as a scum to the surface and is removed. The operation having progressed so far, and the liquid being rendered quite clear, it is kept at a temperature of 88° for about twelve hours, and then carefully ladled into copper crystallising vessels, constructed with the bottom a little higher at one end than at the other. The solution would yield on cooling large crystals of saltpetre, but this is purposely prevented by keeping the liquid in motion by means of stirrers, as as to produce the so-called flour of saltpetre, which is really the salt in a finely-divided state. This is next transferred to wooden boxes termed wash-vessels, 10 feet long by 4 feet wide, provided with a double bottom, the inner one being perforated; between the two bottoms holes are bored through the sides of the vessel and when not required plugged with wooden pegs. Over the flour of saltpetre contained in these wooden troughs, 60 lbs. of a very concentrated solution of pure nitrate of potassa are poured, and allowed to remain for two to three hours, the plugs being left in the holes. The plugs are then removed, the liquor run off, the holes again plugged, and the operation twice repeated, first with a fresh 60 lbs., and next with 24 lbs. of the solution of nitrate of potassa, followed in each case by an equal quantity of cold water. The liquors which are run off in these operations are of course collected, the first being added to the crude saltpetre solution, while the latter, being solutions of nearly pure nitre, are again employed. The saltpetre is next dried at a gentle heat in a shallow vessel, sifted, and packed in casks.

Preparation of Nitrate of Potassa from Chili-saltpetre.

During the last twenty years the preparation of nitrate of potassa from Chili-saltpetre has become an important branch of manufacturing industry. The product obtained by any of the following processes is called "converted-saltpetre," to distinguish it from the preceding preparation. The method of procedure may be one of the following:—

1. The nitrate of soda is decomposed by means of chloride of potassium—

$$\left.\begin{array}{l}\text{100 kilos. of sodic nitrate}\\ \text{87·9 kilos. of potassium chloride}\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{119·1 kilos. potassa nitrate.}\\ \text{68·8 kilos. common salt.}\end{array}\right.$$

MM. Longchamp, Anthon, and Kuhlmann first suggested this mode of preparation, which is now generally used on the large scale, as the decomposition of both salts is very complete, and as the common salt as well as the saltpetre can be utilised. The chloride of potassium is obtained by the decomposition of carnallite, or by means already mentioned.

Equivalent quantities of nitrate of soda and of chloride of potassium are dissolved in water contained in a cauldron of some 4000 litres cubic capacity. As the nitrate of soda of commerce (Chili-saltpetre) does not, as regards purity, vary very much from 96 per cent., some 7 cwts. are usually taken, while of the chloride of potassium, which varies in purity from 60 to 90 per cent., a quantity is taken corresponding, as regards the amount of pure chloride, to the quantity of nitrate of soda. The chloride of potassium is first dissolved, the hot solution being brought to a sp. gr. = 1·2 to 1·21, next the nitrate of soda is added, and the liquid brought, while constantly heated, to a sp. gr. = 1·5. The chloride of sodium continuously deposited is removed by perforated ladles, and placed on a sloping plank so that the mother-liquor may flow back into the cauldron, care being taken to wash this salt afterwards, so as to remove all nitrate of potassa, the washings being poured back into the cauldron. When the liquid in the cauldron has been brought to 1·5 sp. gr.—an aqueous solution of nitrate of potassa at 15°, with a sp. gr. = 1·144, contains 21·074 per cent. of that salt—the fire is extinguished, the liquid left to clear, the common salt still present carrying down all impurities, and when clear it is ladled into crystallising vessels, which being very shallow, the crystallisation is finished in twenty-four hours. The mother-liquor having been run off, the crystals are thoroughly drained and covered with water, which is left in contact with the salt for some seven to eight hours, and then run off; this operation is repeated during the next day; the mother-liquor and washings are poured back into the cauldron at a subsequent operation.

2. Nitrate of soda is first converted into chloride of sodium by means of chloride of barium, nitrate of baryta being formed, and in its turn converted into nitrate of potassa by the aid of sulphate of potassa:—

a. 85 kilos. of nitrate of soda 122 kilos. of chloride of barium	yield	130·5 kilos. nitrate of baryta. 58·5 kilos. of common salt.
β. 130·5 kilos. of nitrate of baryta require for conversion into nitrate of potassa		87·2 kilos. of potassic sulphate, or 69·2 kilos. of potassic carbonate.

When sulphate of potassa is used, permanent-white, baryta-white, or sulphate of baryta is obtained as a by-product, while if carbonate of potassa is used, carbonate of baryta remains, and of course may be readily re-converted into chloride of barium. In order to estimate the advantages of either process, the following points must be kept in view:—*a.* Taking into consideration that it is profitable to convert native carbonate of baryta into chloride of barium—for instance, by exposing witherite to the hydrochloric acid fumes produced in alkali works by the decomposition of salt—and to precipitate an aqueous solution with dilute sulphuric acid to obtain permanent-white, it may be inferred that it will also pay to obtain it as a by-product. *b.* Notwithstanding the complication of this process, it is advantageous as producing a far purer nitrate of potassa.

3. Nitrate of soda is converted by means of potash into the nitrate of that base, pure soda being obtained as a by-product:—

85 kilos. Chili-saltpetre 69·2 kilos. carbonate of potassa	yield	101·2 kilos. of potassic nitrate. 53 kilos. of soda (calcined).

This mode of manufacturing saltpetre was first introduded into Germany during the Crimean War (1854-55) by M. Wöllner, of Cologne, who established large works to prepare saltpetre in this way, and very soon after, during the continuance of the war, five other manufactories of potash-saltpetre had been established on this method. In 1862 the production amounted to 7,500,000 lbs. of potash-saltpetre, the carbonate of potassa required being obtained from beet-root molasses, the soda resulting as a by-product being even superior to that produced by Leblanc's process.

4. Nitrate of soda being decomposed by caustic potassa yields potassic nitrate and caustic soda.

According to M. Lunge's description, this process, first suggested by MM. Landmann and Gentele, afterwards modified by M. Schnitzer, and practically applied by M. Nöllner, is carried on in Lancashire in the following manner:—There is added to a caustic potash lye of 1·5 sp. gr., containing about 50 per cent. of dry caustic potassa, an equivalent quantity of nitrate of soda, and the whole, after a short time, crystallised. The nitrate of potassa having been separated from the mother-liquor, that fluid, the density of which has been greatly decreased by the reaction, is by evaporation again brought to its former density, and yields on cooling another crop of crystals of potash-saltpetre. Usually there then only remains a solution containing caustic soda with saline impurities; sometimes, however, a third crop of crystals is obtained. The deposit during the evaporation is chiefly carbonate of soda derived from the chloride of sodium contained in the potassium chloride from which the caustic potassa is made, this chloride being also converted into carbonate. The small quantities of undecomposed chlorides of potassium and sodium and sulphate of lime are retained in the mother-liquor, which is evaporated to dryness and ignited, yielding a dry caustic soda of a bluish-colour. The crystallised nitrate of potassa is now carefully refined to remove all impurities to about 0·1 per cent. of chloride of sodium, converted into saltpetre-flour, and treated as already described. Notwithstanding that the various operations have been carried on in iron vessels, the salt does not contain any of this metal, nor is the colour in any way affected. The flour is dried in a room 2 metres wide by 5 metres in length, built of brick-work, similarly to the chloride of lime rooms, and having a pointed arched roof 2 metres in height. The saltpetre-flour is spread on a wooden floor, under which extends a series of hot-air pipes, keeping the temperature at 70°, and very rapidly effecting the drying.

Testing the Saltpetre. If, when perfectly pure, saltpetre is carefully fused, and allowed to cool, it becomes a white mass, exhibiting a coarsely radiated fracture; even so small a quantity as $\frac{1}{50}$th of chloride of sodium causes the fracture to appear somewhat granular; with $\frac{1}{40}$th the centre is not at all radiated, and is less transparent; and with $\frac{1}{30}$th the radiation is only slightly perceptible at the edges of the fracture. Nitrate of soda has the same effect. This method of testing the purity of nitre, due to M. Schwartz, is employed in Sweden, where every landowner pays a portion of his taxes in saltpetre of a specified degree of purity. A great number of methods of testing saltpetre have been suggested by various authors for the purposes of the manufacture of gunpowder, not, however, in sufficiently general use to interest the reader. Werther's test for chlorine and sulphuric acid is by solutions of the nitrates of baryta and silver; the silver solution is such that each division of the burette corresponds to 0·004 grm. of chlorine, and with the baryta solution to 0·002 grm. of sulphuric acid. According to Reich's plan, 0·5 grm. of dried and pulverised saltpetre is ignited to a dull red heat, with from 4 to 6 times its weight of pulverised quartz; the nitric acid is expelled, the loss of weight consequently indicating the quantity, the sulphates and chlorides not being decomposed at a dull red heat. If the loss $= d$, we have 1·874 *d* nitrate of potassa, or 1·574 *d* nitrate of soda.

Quantitative Estimation of the Nitric Acid in Saltpetre. This method, due to Dr. A. Wagner, is based upon the fact that when saltpetre, or any other nitrate, is ignited, access of air being excluded, with an excess of oxide of chromium and carbonate of soda, the nitric acid oxidises the chromic oxide according to the formula $Cr_2O_3 + NO_5 = 2CrO_3 + NO_2$. 76·4 parts, by weight, of oxide of chromium are oxidised to chromic acid by 54 parts of nitric acid, or of 1 of chromic oxide by 0·7068 of nitric acid. The operation is performed by taking from 0·3 to 0·4 grm. of the nitrate, mixing it intimately with 3 grms. of chromic oxide and 1 grm. of carbonate of soda, introducing this mixture into a hard German glass combustion-tube, one end of which is drawn out, and a vulcanised india-rubber tube attached to it, which is made to dip for about a quarter of an inch into water, while to the other open end, by means of a cork and glass tube bent at right angles, an apparatus is fitted for the evolution of carbonic acid gas, which is made to pass through the tube before igniting it, and kept passing through all the time until the tube is quite cool again after ignition. The contents of the tube are placed in warm water, and after filtration the chromic acid is estimated by Rose's method. This process of estimating nitric acid has been found to yield very accurate results.

Uses of Saltpetre. This salt is employed for many purposes, the most important being:—1. The manufacture of gunpowder. 2. The manufacture of sulphuric and nitric acids. 3. Glass-making, to refine the metal as it is termed. 4. As oxidant and flux in many metallurgical operations. By the ignition of 1 part of nitre and 2 of argol, in some cases refined argol (cream of tartar), *black flux* is formed consisting of an intimate mixture of carbonate of potassa and finely divided charcoal. The ignition of equal parts of saltpetre and cream of tartar gives *white flux*, consisting of a mixture of carbonate of potassa and undecomposed saltpetre; both these mixtures are often used. Black flux may also be made by intimately mixing carbonate of potassa with lamp-black and white flux. 5. When mixed with common salt and some sugar in the salting and curing of meat. 6. For preparing fluxing and detonating powders. Baumé's fluxing powder is a mixture of 3 parts of nitre, 1 of pulverised sulphur, and 1 of sawdust from resinous wood; if some of this mixture be placed with a small copper or silver coin in a nutshell and ignited, the coin is melted in consequence of the formation of a readily fusible metallic sulphuret, while the nutshell is not injured. Detonating powder is a mixture of 3 parts saltpetre, 2 carbonate potassa, and 1 pulverised sulphur; this powder when placed on a piece of sheet-iron, and heated over a lamp, will explode with a loud report, yielding a large volume of gas:—

$$\left.\begin{array}{l}\text{Saltpetre, } 6KNO_3,\\ \text{Potassic carbonate, } 2K_2CO_3,\\ \text{Sulphur, } 5S.\end{array}\right\} = \left\{\begin{array}{l}\text{Nitrogen, } 6N.\\ \text{Carbonic acid, } 2CO_2.\\ \text{Sulphate of potassa, } 5K_2SO4.\end{array}\right.$$

7. For manure in agriculture. 8. In many pharmaceutical preparations. 9. For the preparation of Heaton steel.

Sodic Nitrate. This salt, also known as cubical saltpetre, Chili-saltpetre, nitrate of soda, $NaNO_3$, containing in 100 parts 36·47 soda, and 63·53 parts nitric acid, is found native in the district of Atacama and Tarapaca, near the port of Uquique, in Peru, in layers termed *caleche* or *terra salitrosa*, 0·3 to 1·0 metre in thickness, and extending over more than 150 miles, nearly to Copiapo, in the north of Chili. The deposit chiefly consists of the pure, dry, hard salt, and is close to the surface of the soil. It is also found in other parts of Peru mixed with sand, in some places close to the surface of the soil, in others at a depth of 2·6 metres. Valparaiso being the great exportation dépôt for Peru, Bolivia, and Chili, both surface and deep soil salts are met with in tthe rade of that important port. The unrefined Chili-saltpetre is crystalline, brown or yellow, and somewhat moist; but the salt sent to the European markets is commonly semi-refined by being dissolved in water and evaporated to dryness. The composition of a sample in 100 parts is:—

Nitrate of soda	94·03
Nitrate of soda	0.31
Chloride of sodium	1.52
Chloride of potassium	0·54
Sulphate of soda	0·92
Iodide of soda	0·29
Chloride of magnesium	0·96
Boric acid	traces
Water	1·96
	100·00

Being deliquescent the salt is not employed in the manufacture of gunpowder, but may be used for blasting powder. It is largely used for the preparation of sulphuric and nitric acids; for purifying caustic soda; for making chlorine in the manufacture of bleaching powders; for the preparation of arseniate of soda; in the curing of meat; glass-making; in the preparation of red-lead; in large quantities in the conversion of crude pig-iron into steel, by Hargreaves's and by Heaton's processes; for preparing nitrate of potassa; and for the preparation of artificial manures and composts, it being used unmixed as a manure for grain crops.

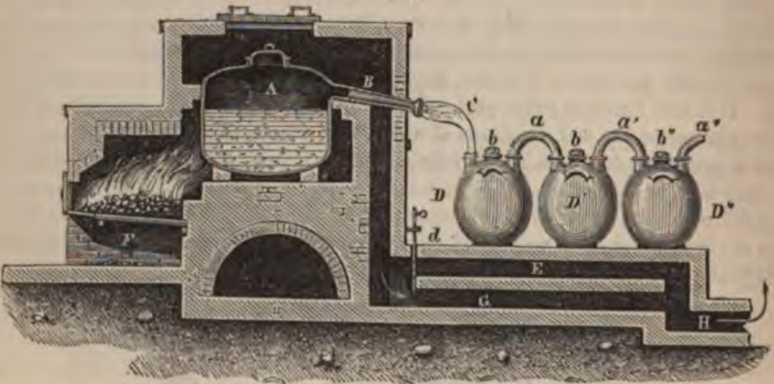
It may be seen from the analysis of nitrate of soda quoted above that that salt contains a small quantity of iodine, which at Tarapaca is extracted from the mother-liquor remaining from the re-crystallisation. According to M. L. Krafft the iodine amounts to 0·59 grm. in 1 kilo. of crude nitrate; 40 kilos. of iodine being prepared per day. M. Nöllner thinks that the formation of the nitre deposits in Chili and other parts of South America has taken place under the influence of marine plants containing iodine. In order to give some idea of the large and increasing exportation of Chili-saltpetre, we quote from the published statistics, that in 1830, 18,700 cwts., and in 1869, 2,965,000 cwts., were shipped.

NITRIC ACID.

Methods of Manufacturing Nitric Acid.

This acid (NHO_3) is generally manufactured by decomposing nitrate of soda by sulphuric acid, and condensing the vapours set free. It is obtained on the large scale by placing in a cast-iron vessel, A, Fig. 65, the nitrate to be operated upon, to which is added by means of a funnel strong sulphuric acid. The lid is replaced, and the vessel connected by means of the clay-lined tube B, with the glass tube, C, dipping into the large stoneware flask, D, which serves the purpose of a receiver. This flask is connected by means of a tube, *a*, to a similar vessel, D′, and that to a third vessel, D″, and so on, in order to completely condense the vapours which might have escaped through the first, second, and third vessels. The iron vessel, A, is heated by means of the fire placed in the hearth, F, the smoke and hot gases being carried off by G H. At the outset of the operation the damper, *d*, is so regulated as to shut off the lower channel, and cause the smoke and hot gases to pass through E, heating the vessels D, D′, and D″, this precaution being

FIG. 65.



required to prevent their cracking by the hot acid vapours entering from A. As soon, however, as the distillation has fairly commenced, the damper is altered to shut off E, and pass the hot air and gases through G. The nitric acid condensed in the first receiver is sufficiently strong for immediate use, but to facilitate the condensation some water has been poured through the openings *b′ b″*, into the other receivers, the acid from which is weaker and known in the trade as aquafortis.

Very frequently the distillation of nitric acid is conducted in a series of glass retorts placed on a sand-bath; there are generally two rows of retorts, the heating apparatus being a galley oven. If the acid is to be pure, the first condensations are collected in separate receivers, as the acid first condensed contains hydrochloric acid due to the chlorides contained in the nitrates under operation.

The proportion of materials employed is:—

30 kilos. of Nitrate of potassa to 29 kilos. of strong sulphuric acid; or,
17 ,, Nitrate of soda to 14·5 ,, ,, ,, ,,

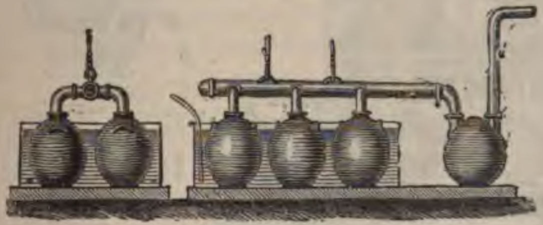
The bisulphate of soda which remains may either be used for the preparation of fuming sulphuric acid, or may be mixed with common salt, and ignited, to produce hydrochloric acid and neutral sulphate of soda, available in the preparation of sodic carbonate.

The nitric acid (NHO_3) resulting from the above operation is a colourless, transparent fluid, having a sp. gr. of 1·55, and boiling at 80°. When diluted with water the boiling-point is higher. An acid containing 100 parts (NHO_3) and 50 parts of water boils at 129°, but if the dilution with water is carried further the boiling-point is again lowered; consequently, when such an acid is heated above 100° the result is that at first water with only a trace of acid distils over, and if the process be continued the boiling-point gradually increases until it reaches 130°, when there distils over what is termed double aquafortis, sp. gr. = 1·35 to 1·45, ordinary or single aquafortis having a sp. gr. = 1·19 to 1·25. Nitric acid, when in contact with air, emits fumes, owing to the absorption of water from the atmosphere.

Bleaching Nitric Acid.

The stronger acid manufactured as described is usually of a yellow colour, due to the presence of hyponitric acid. If a colourless acid is desired, the crude acid must be submitted to a bleaching operation, consisting of the following:—The coloured acid is poured into large glass vessels placed (Fig. 66) in a water-bath, heated to 80° to 90°, and left in these vessels as long as any coloured vapours are given off. The escaping hyponitric acid is carried by means of glass or glazed earthenware tubes either into a sulphuric acid chamber and there utilised, or into the flue of a chimney, and thus into the air. Any hydrochloric acid present in the nitric acid is also carried off as chlorine. In order to remove any sulphuric acid it

FIG. 66.

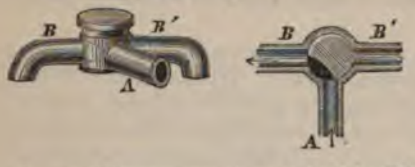


is necessary to distil the nitric acid over pure nitrate of baryta, while the last traces of hydrochloric acid can be removed by distillation over pure nitrate of silver.

Condensation of the Nitric Acid.

More recently improvements have been made in the manufacture of nitric acid, bearing especially upon the possibility of omitting the bleaching process, and a better mode of condensing the vapours of the acid. The first point is supplied by an arrangement introduced in the manufactory of M. Chevé, in Paris. Every practical chemist knows that the red vapours appear only at the outset and towards the end of the distillation of the nitric acid, and it is therefore only required to distil fractionally to obtain on the one hand a red-coloured acid, the *acidum nitroso-nitricum* or *acidum nitricum fumans fortissime* of the pharmaceutists, and on the other a colourless acid, which can be forthwith delivered to the consumer. In order to practically effect the fractional distillation, a tap of porcelain or hard-fired stoneware, constructed as exhibited in Fig. 67, is fixed by means of A, in communication with the iron distilling vessel, while the tubes B and B are connected with two different receivers. The tap is bored in such a manner, that at pleasure either the communication between A and B′, or the communication between A and B, can be established. By proper management, therefore, it is possible to separate the red-coloured acid entirely, and without any additional expense, from the colourless acid.

Fig. 67.



A second improvement, contrived by MM. Plisson and Devers, Paris, bears upon the condensation apparatus, which consists in their works of a battery of ten peculiarly constructed bottles, six of which are open at the bottom and funnel-shaped, so as to fit in the necks of large carboys, G, Fig. 68. From a cylinder not shown in the engraving, being hidden by the wall, M, a stoneware tube is connected with

Fig. 68.

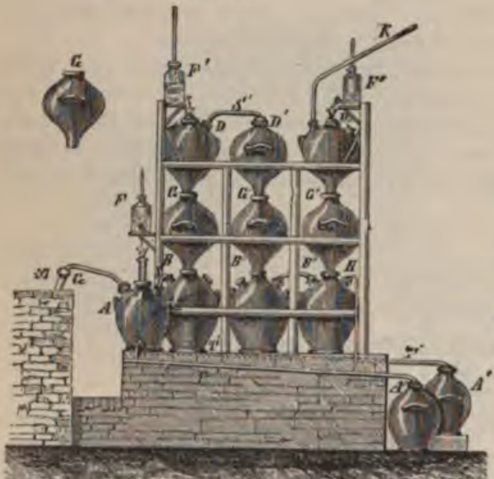


Fig. 69.

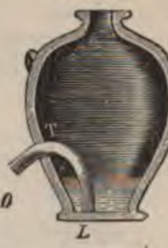
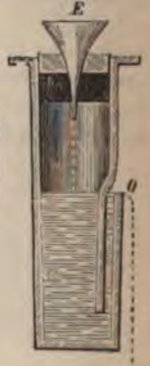


Fig. 70.



the bent glass tube, G, which communicates with one of the three tubulatures of the first carboy, A, which serves to collect the acid, that, by the boiling over of the mixture in the iron vessel, has been rendered more or less foul. The carboy A is provided with a small tube, T, arranged to act as a hydraulic valve in such a manner that, when the fluid in the carboy has risen to a height of some centimetres, any additional fluid entering A is carried off into the well-stoppered carboy A′. The second tubulature of the carboy A is fitted with a funnel through which water flows from the bottle F into A, thereby aiding the condensation. The acid vapours pass through the curved glass tube F, into the carboy B, from which, as likewise from the carboys B′ and B″, the condensed fluid is carried by the tube T into the carboy A″. Any vapours which escape condensation in B are carried off to C, and thence to D, a portion of the acid being condensed in each of the vessels, and flowing back first to B and then to A″. Any vapour not condensed in C and D is conducted by the glass tube G, first to D′, next to C″, and finally to B, where condensation takes place. Any vapours not now condensed are carried to B″, C″, D″, and finally to the chimney stalk. The Mariotte botttles F′ and F″ contain water, which flows into the condensing vessels and dilutes the acid to 36° B. (= 1·31 sp. gr. = 42·2 per cent. N_2O_5). In order to reduce any pressure arising in the vessels A′ and A″, a tube H, and a similar one not represented in the cut, are connected with T and T′, for the purpose of carrying any non-condensed vapour into B″, where these vapours collect.

Although this apparatus appears complicated, the working is very readily managed. The acid vapours issuing from the distillatory apparatus are partly condensed in the vessel A, and thence carried to A′, the vapours still uncondensed continuing their course to B, B′, B″, the fluid there collected flowing back to the general receiver A″. This apparatus when once well put together, has rarely to be repaired, saves much labour, and produces a larger quantity of acid than the ordinary apparatus, this being due to the more complete condensation; while by the ordinary method only 125 to 128 kilos. of nitric acid are obtained from 100 kilos. of nitrate, the quantity obtained by this apparatus amounts to 132 to 134 kilos. The following brief description, illustrated by Figs. 69 and 70, will explain the internal construction of the bottles and of the syphon funnel. In each of the carboys of the lowest row is inserted a bent stoneware tube, T, Fig. 69, the opening, O, of which is outside the bottle; a narrow space, L, admits the fluid to the interior of the tube, and it is clear that the acid can only attain a certain height in the carboy. The syphon funnel consists of a stoneware tube about 3 centims. in diameter, the side of which, Fig. 70, is perforated in a longitudinal direction; any fluid therefore flowing into this tube from E can only reach to the opening O.

Other Methods of Nitric Acid Manufacture.

The following methods, differing from that above described, must here be mentioned; but the reader should not infer that they are actually in practice:—1. Action of chloride of manganese (chlorine preparation residues) upon nitrate of soda. When a mixture of these salts is heated to about 230°, nitrous vapours ($NO_2 + O$) are evolved, and there remains oxide of manganese, which can be again employed in the manufacture of chlorine.

$$\left.\begin{array}{c}5MnCl_2\\ \text{and}\\ 10NaNO_3\end{array}\right\}\text{ yield }\left\{\begin{array}{l}(2MnO + 3MnO_2),\\ 10NaCl,\\ 10NO_2 + O,\end{array}\right.$$

By causing the mixture of hyponitric acid and oxygen to come into contact with water in the condensing apparatus nitric acid results, the excess of hyponitric acid being decomposed into nitric acid and deutoxide of nitrogen. If the quantity of air in the apparatus is sufficiently large to oxidise the entire bulk of the nitrogen deutoxide into nitric acid this process is continuous, but if there is not enough air, the deutoxide of nitrogen is dissolved in the nitric acid, any excess of that gas escaping. From the experiments on this process by Dr. Kuhlmann, who used clay retorts, it appears that 100 parts of nitrate of soda yield from 125 to 126 parts of nitric acid at 35° B.; this result almost agrees with that obtained by the ordinary process. Dr. Kuhlmann also instituted experiments with other chlorides, viz., those of calcium, magnesium, and zinc, the result being the formation of nitric acid and chloride of sodium with lime, magnesia, and oxide of zinc.

2. Action of certain sulphates upon alkaline nitrates. Dr. Kuhlmann has proved by a series of experiments that the sulphates, including only those having no acid properties, decompose the alkaline nitrates. Sulphate of manganese decomposes nitrate of soda, the result being the formation of products similar to those when chloride of manganese is employed; similar reactions take place when sulphate of zinc, sulphate of magnesia, and gypsum are used for this purpose.

3. From nitrate of soda and carbon, yielding soda and nitric acid.

4. From nitrate of soda and silica or alumina, yielding nitric acid, silicate of soda and soda.

5. From nitrate of baryta and sulphuric acid, without distillation; the nitric acid (= 10° to 11° B.) decanted from the sulphate of baryta (permanent white) can be concentrated by boiling to 25° B.

Density of Nitric Acid. According to Kolb, the specific gravity of nitric acid bears to the quantity of concentrated acid contained the following relation:—

100 parts contain		Density.	
NHO_3.	N_2O_5.	at 0°.	at 15°C.
100·00	85·71	1·559	1·530
97·00	83·14	1·548	1·520
94·00	80·57	1·537	1·509
92·00	78·85	1·529	1·503
91·00	78·00	1·526	1·499
90·00	77·15	1·522	1·495
85·00	72·86	1·503	1·478
80·00	68·57	1·484	1·460
75·00	64·28	1·465	1·442
69·96	60·00	1·444	1·423
65·07	55·77	1·420	1·400
60·00	51·43	1·393	1·374
55·00	47·14	1·365	1·346
50·99	43·70	1·341	1·323
45·00	38·57	1·300	1·284
40·00	34·28	1·267	1·251
33·86	29·02	1·226	1·211
30·00	25·71	1·200	1·185
25·71	22·04	1·171	1·157
23·00	19·71	1·153	1·138
20·00	17·14	1·132	1·120
15·00	12·85	1·099	1·089
11·41	9·77	1·075	1·067
4·00	3·42	1·026	1·022
2·00	1·71	1·013	1·010

The following table exhibits comparative data of density and degrees according to Baumé:—

Degrees according to Baumé.	Density.	100 parts contain at 0°		100 parts contain at 15° C.	
		NHO_3.	N_2O_5.	NHO_3.	N_2O_5.
6	1·044	6·7	5·7	7·6	6·5
7	1·052	8·0	6·9	9·0	7·7
9	1·067	10·2	8·7	11·4	9·8
10	1·075	11·4	9·8	12·7	10·9
15	1·116	17·6	15·1	19·4	16·6
20	1·161	24·2	20·7	26·3	22·5
25	1·210	31·4	26·9	33·8	28·9
30	1·261	39·1	33·5	41·5	35·6
35	1·321	48·0	41·1	50·7	43·5
40	1·384	58·4	50·0	61·7	52·9
45	1·454	72·2	61·9	78·4	72·2
46	1·470	76·1	65·2	83·0	71·1
47	1·485	80·2	68·7	87·1	74·7

47° B.	correspond to	96°	Twaddle.
46° ,,	,,	92°	,,
45° ,,	,,	88°	,,
43° ,,	,,	84°	,
42° ,,	,,	80°	,,
38° ,,	,,	70°	,,
34° ,,	,,	60°	,,
29° ,,	,,	50°	,,
25° ,,	,,	40°	,,
20° ,,	,,	30°	,,
14° ,,	,,	20°	,,
7° ,,	,,	10°	,,

Nitric acid of	1·52	sp. gr. boils at	86°
,,	1·50	,,	99°
,,	1·45	,,	115°
,,	1·42	,,	123°
,,	1·40	,,	119°
,,	1·35	,,	117°
,,	1·30	,,	113°
,,	1·20	,,	108°
,,	1·15	,,	104°

Fuming Nitric Acid. When in the preparation of nitric acid there is taken for 1 molecule of nitrate of potassa 1 molecule of sulphuric acid, there is obtained by distillation a reddish-yellow fluid, consisting of a mixture of nitric and hyponitric acids, known as red fuming nitric acid. When equal molecules of nitrate of potassa and sulphuric acid are taken, only one-half of the quantity of nitric acid is expelled, while the other half is decomposed into hyponitric acid and oxygen, the former combining with the nitric acid, and forming the fuming nitric acid. When in the preparation of nitric acid by the decomposition of the potassium or sodium nitrate, two molecules of sulphuric acid are employed, all the nitric acid in these salts is obtained, and there remains in the retort bisulphate of either base. When nitrate of soda is employed, it is, owing to the easier decomposition of this salt by sulphuric acid, not necessary to use exactly 2 molecules of sulphuric acid; 1·25 to 1·50 molecules of that acid have been found to be practically sufficient. 100 parts of Chili-saltpetre yield 120 to 130 parts of nitric acid at 36° B.

The red fuming nitric acid is now generally prepared by adding to the ordinary concentrated nitric acid a substance which effects its decomposition. Sulphur has been employed for this purpose, but starch is generally used, and, according to M. C. Brunner's recipe, in the following manner:—To 100 parts of saltpetre, 3½ parts of starch are added, and placed in a capacious retort, into which is poured 100 parts of strong sulphuric acid, sp. gr. = 1·85. The distillation usually sets in without the aid of heat, but towards the end of the operation the application of a gentle heat is required. 100 parts of nitrate of potassa yield by this method about 60 parts of fuming nitric acid. The retort in this operation should not be filled to more than one-third of its capacity, owing to the very strong evolution of gas which takes place.

Uses of Nitric Acid. The technical application of nitric acid is based on its property of oxidation when in contact with certain substances, the acid splitting up into deutoxide of nitrogen, hyponitric acid, and ozone, the latter forming with the body which caused the decomposition of the acid either an oxide or a peculiar compound, while the hyponitric acid, when organic substances are present capable of combining with it, forms the nitro-compounds, nitrobenzole, nitronapthaline, nitroglycerine, nitromannite, nitrocellulose, or gun-cotton, &c. A large number of metals are soluble in moderately concentrated nitric acid, but the strongest acid fails to act upon iron and lead. Proteine compounds, albumen, the skin of the hands, silk, horn, feathers, &c., are stained yellow by nitric acid, hence the use of this acid in dyeing silk. If the acid is in contact with these substances for any length of time, they are completely decomposed, and partly converted into picric acid. Starch, cellulose, and sugar are converted by the action of nitric acid into oxalic acid; but very dilute nitric acid converts starch into dextrine, and concentrated acid into xyloidine. Owing to the property nitric acid possesses of destroying certain pigments—for instance, indigo—it is sometimes employed in calico printing to produce a yellow pattern on an indigo ground. This acid is also used in dyeing woollen materials; in hat-making, to prepare a mercurial solution used in dressing felt hats; in the manufacture of sulphuric acid; in the preparation of lacquers; in the preparation of nitrate of iron, a mordant used in dyeing silk black; for preparing picric acid from carbolic acid, and naphthaline-yellow from naphthaline; in the manufacture of nitrobenzol, nitrotoluol, and phthalic acid; and for the preparation of nitrate of silver, arsenic acid, fulminate of mercury nitroglycerine, dynamite, &c.

TECHNOLOGY OF THE EXPLOSIVE COMPOUNDS.

a. Gunpowder, and the Chemistry of Fireworks, or Pyrotechny.

On Gunpowder in General. The substance known as gunpowder, or simply as powder, is a more or less finely granulated mechanical mixture of saltpetre, sulphur, and charcoal, the quantities of these materials being properly defined. It ignites at 300°, also when touched with a red-hot or burning body, or under certain conditions by friction or a sudden blow. Powder under these conditions burns off rapidly but not instantaneously, yielding as the products of its combustion nitrogen, carbonic acid, or carbonic oxide, while there remains a solid substance consisting of a mixture of sulphate and carbonate of potassa. When the powder is ignited in a closed vessel, the sudden evolution of the large volume of gases causes a pressure impossible to be withstood; and even in guns and large ordnance, in which one side of the vessel is formed by the yielding shot, the metal forming the other sides must possess great elasticity. In guns and artillery the pressure only lasts as long as the ball is inside the gun, therefore the slower the combustion of the powder through its entire mass, the lower is the velocity of the projectile.

Manufacture of Gunpowder. It is essential that the materials employed in the manufacture of powder should be very pure; the saltpetre should not contain any chlorides; the sulphur should be free from sulphurous acid, hence not flowers of sulphur but refined roll sulphur is used; and lastly the charcoal requires very great attention. The wood from which it is intended to prepare a charcoal for gunpowder should be such as yields the least possible quantity of ash, while the charcoal should be soft like that used in pharmacy. The stems of the hemp and flax plants, especially the former, yield excellent charcoal, but in consequence of the limited supply, the wood of the wild plum tree (*Prunus padus*) is largely used in Germany, France, and

Belgium; and in England the lime, willow, poplar, horse-chestnut, vine, hazel, cherry, alder, and other light white woods are employed for this purpose. All these varieties yield on being carbonised—effected in various ways, in retorts similar to those used in gas-works, in pits dug in the earth, by the aid of superheated steam, the wood being placed in boilers, &c.—from 35 to 40 per cent. charcoal. The temperature during the progress of carbonisation being kept as low as possible, there is obtained a very soft reddish-brown charcoal, known as *charbon roux*. The charcoal prepared in cylindrically-shaped retorts is very inappropriately designated distilled charcoal.

Mechanical Operations of Powder Manufacture. These operations include:—

1. The pulverising of the ingredients. 2. The intimate mixing of these substances. 3. The moistening of the mixture. 4. The caking or pressing. 5. The granulation and sorting of the grain, as it is termed. 6. Surfacing the powder. 7. Drying. 8. Sifting from the dust.

Pulverising the Ingredients. This operation can be performed in three different ways:—

a. By means of revolving drums.
b. By mill-stones; or
c. In stamping-mills.

a. The pulverisation by means of revolving drums is an invention due to the French revolution, and has the advantages of being very effective, rapid in execution, and of preventing the flying about of the ingredients in a fine dust. The drums are made of wood, lined with stout leather, and provided with a series of projections. The substance to be pulverised is put into the drum with a number of bronze balls of about ¼ inch diameter, their action aided by that of the projections, when the drum is turned on its horizontal axis at a moderate speed, soon effecting a reduction to a fine powder. The charcoal and sulphur are separately pulverised; the saltpetre being obtained as a flour. (See Saltpetre.)

b. Grinding by the aid of mill-stones. Two heavy vertical stones, similar to those in use for crushing linseed, revolve on a fixed horizontal stone. This contrivance is the most frequently used.

c. Stampers are now employed only in small powder-mills. Frequently 10 to 12 stamps made of hard wood are placed in a row, each stamp being fitted with a bronze shoe, the entire weight being about 1 cwt. The stamps are moved by machinery, and make from 40 to 60 beats a minute. The materials to be pulverised are placed in mortar-shaped cavities in a solid block of oak wood, each cavity containing 16 to 20 lbs. In Switzerland hammers instead of the stampers are employed.

Mixing the Ingredients. The mixing is performed by the aid of drums similar in size and shape to those used in the pulverisation, but made of stout leather instead of wood. The mixing of 100 kilos. of the ingredients, aided by the action of 150 bronze balls, takes fully three hours, the drum making ten revolutions a minute. It is usual to moisten the materials with 1 to 2 per cent. of water, supplied by fine jets regulated by taps.

When stampers and mill-work are employed, the sulphur and charcoal are first separately pulverised by 1000 blows, and saltpetre having been mixed with these ingredients in the proper proportion, the machinery is again set in motion, and at first, after every 2000 blows, and then after every 4000 blows, the contents of the stamp-holes are removed from the one to the other, this operation being repeated some six or eight times. Where drums are used for the mixing operation, the moistening takes place after the mixture has been removed to a wooden trough, where 8 to 10 per cent. of its weight of water is added, care being taken to stir with a wooden spatula.

Caking or Pressing the Powder. This operation, which in stamping-mills is the last of a continuous series, is separately performed where other machinery is employed. In the French and German powder-mills, the compression is effected in a rolling-mill, the rollers having a diameter of 0·6 metre. The lower roller is made of wood, the upper of bronze; between the two an endless piece of stout linen is arranged, and upon this the moist powder is placed. The cakes are 1 to 2 centims. in thickness, with the hardness and very much the appearance of clay-slate.

The operation of pressing is of great importance; the stronger the pressure the greater the quantity of active material present in a given bulk, and hence the larger the volume of gas given off by the ignition of the powder. In many English powder-mills the pressing is effected by very powerful hydraulic machines, because, within certain limits, the more the materials are pressed, the more slowly the powder burns, when finished, while the temperature of ignition being lower, the expansion of the gases is less. If the powder were finished either without having undergone any pressure at all, or with only a slight pressure, it would act as a detonating-powder, the decomposition being instantaneous throughout its entire mass.

Granulation of the Cake, and Sorting the Powder. The conversion of the cake into granules is effected—

1. By means of sieves.
2. By means of peculiarly-constructed rollers, Congreve's method; or
3. According to Champy's method.

The granulation of gunpowder by the aid of sieves is carried on in the following manner:—The sieves consist of a circular wooden frame, across which a piece of parchment is stretched perforated with holes; the sieves are distinguished according to their uses, and by the size of these holes; that employed for breaking up the cake having larger holes, and bearing a name different from the sieves used to produce the granules; this sieve again being distinguished from that employed for sorting the powder into the variously sized grain as commercially known. The sieves are provided with a so-called rummer, a lens-shaped disc made of hard wood, guaiac, box, or oak-wood, motion being imparted to the sieves by hand if they are small, or by suitably arranged machinery if they are large, in which case Lefebvre's granulating-machine fitted with eight sieves in an octagonal wooden frame is generally employed.

Congreve's granulating-machine consists of three pairs of brass rollers, 0·65 metre in diameter, provided with diamond-shaped projections 2 millimetres high, the projections of the upper rollers being coarser than those of the others. The broken-up cake is conveyed to the upper rollers by means of an endless canvas sheet. The mode of feeding this sheet is somewhat peculiar and ingenious: the loose bottom of a square box filled with coarsely-pounded cake is made to rise slowly upwards, and discharge the cake uniformly upon the sheet through an opening in the side of the box. The cake while passing through the rollers is granulated, and then showered upon two sets of wire-gauze sieves to which a to-and-fro motion is imparted. Below these sieves again is a frame containing wire-gauze, the meshes of which are too small to admit of the passage of ordnance powder, while the dust and cartridge-powder readily fall through upon another wire-gauze, the meshes of which retain the rifle-powder but let the dust pass. The quantity of dust made by the Congreve machine is very small, owing to the fact that the rollers do not crush but break the cake. Champy's method, by which a very round-grained powder is obtained, is performed in the following manner:—Through the hollow axis of a wooden drum a copper tube, perforated with very small holes, is carried, and from these holes water spouts in a fine spray upon the broken-up powder-cake placed in the drum, to which a comparatively rapid motion is imparted. Each drop of water forms the nucleus of a grain of powder, which is constantly increasing in size by being turned round in the midst of a mass of damp powder-cake; the rotation of the drum is discontinued as soon as the grain has attained a sufficient size. The powder thus obtained is almost perfectly globular, but not of the same size; the sorting is effected by means of sieves, the oversized grains being returned to the drum, as well as the undersized grains, which become the nuclei of proper-sized grain. According to the Berne method, round-grained powder is prepared by causing the angular-shaped powder to be rotated in stout linen-bags; but by this plan much dust is formed.

Polishing the Granulated Powder. The aim of this operation is to impart symmetry to the grain, and to separate all the dust. It is performed in drums similar to those described above; 5 cwts. of the powder is polished at a time, the drums rotating slowly for a few hours.

In some countries the polishing is effected by placing the powder in casks internally provided with quadrangular rods. In Holland, Dr. Wagner states that some black-lead is added to the powder during this operation to prevent ignition, but this is not generally done. Highly-polished powder does not readily attract moisture, and is to be preferred in a very damp climate.

Drying the Powder. It is clear that this operation requires very great care in more than one respect. In small powder-works the powder is sometimes dried by exposure to the heat of the sun, being spread out on canvas sheets stretched in wooden frames; or the drying-room is heated by a stove. In large powder-mills other methods of drying the powder are general.

The quality of the powder very much depends on the care bestowed upon the drying. A too rapid drying entails the following disadvantages:—*a*. The powder may be very wet and not polished; coarse ordnance and ordinary military powder is never polished, and hence blackens the hands: while, although the water is driven off, the nitre is carried to the surface of the grain, which thereby cakes together. *b*. By the too rapid evaporation of the water, channels and cracks are made in the grain, impairing its density, increasing its bulk, and rendering it more hygroscopic. *c*. Lastly, rapid drying entails a large amount of dust. For these reasons gunpowder, before being placed in the drying-rooms, is exposed for some time to a gentle heat in a well-ventilated room, the heat from a waste steam-pipe being sufficient.

Sifting the Dust from the Powder. Having been dried, the powder is sometimes glazed, as it is termed; that is to say, again polished in the manner above described; but generally this second polishing is dispensed with, and the dry powder cleansed from the dust which adheres to it, by being placed in bags, made of a peculiar kind of woollen fabric, and arranged in frame-work to which a to-and-fro motion is given by machinery, the fine dust passing between the threads of the fabric into a box. The loss thus occasioned amounts on an average to 0·143 per cent., the dust consisting chiefly of charcoal.

Properties of Gunpowder. Good powder is recognised by the following properties:—1. Its colour should be slate-black; when blue-black it indicates that the powder contains too much charcoal, while a deep black colour shows the powder to be damp. If the charcoal employed was the so-called *charbon roux*, the colour of the powder will be a brown-black. 2. It should not be too much polished so as to shine like burnished black-lead. Small shining specks indicate that the saltpetre has crystallised on the surface. 3. The grains should be uniform in size, unless, of course, two differently-sized powders have been mixed. 4. The grain should crack uniformly when strongly pressed, should withstand pressure between the fingers, and should not be readily crushed to powder when pressed between the hands. 5. When pulverised the mass should feel soft; hard sharp specks show that the sulphur has not been well pulverised. 6. Powder should not blacken the back of the hands or a sheet of white paper when gently rubbed. If it does so, there is either powder-dust or too much moisture. 7. When a small heap of powder is ignited on paper the combustion should be rapid, completely consuming the powder, and not setting fire to the paper. If black specks remain, the powder either contains too much charcoal, or it is an indication that that substance has been badly incorporated with the rest of the materials. Yellow streaks left after the ignition show the same defects for the sulphur. If no grains of powder remain, it is a proof that the powder was not well mixed; when any remaining grains of powder cannot be separately ignited, the saltpetre used was impure. If the powder on being ignited sets fire to the paper, it is a proof that it is either damp or of very inferior quality.

The fact that different kinds of powder, although of the same weight to the cubic foot, do not have the same specific gravity, is shown by the following table:—

	1 cubic foot in pounds weight.	Sp. gr
Neisse's ordnance powder	60	1·77
" " " (new mill)	60	1·67
Berlin ordnance powder	60	1·63
Russian ordnance powder	60$\frac{5}{16}$	1·56
Berne ordnance powder (No. 6)	59$\frac{3}{8}$	1·67
Berlin rifle powder (new mill)	60	1·63
Berne rifle powder (No. 4)	60$\frac{3}{8}$	1·67
Hounslow rifle powder	59	1·72
Berlin sporting powder (old mill)	62	1·77
Le Bouchet's sporting powder	59$\frac{1}{4}$	1·87
Very coarse-grained ordinary Dutch powder ..	60$\frac{1}{16}$	1·87
Very coarse-grained ordinary Austrian powder	64$\frac{3}{8}$	1·72

Gunpowder can absorb more than 14 per cent. of moisture from the air; if the quantity of water thus taken up is not above 5 per cent., the powder, on being gently dried, reassumes its former activity; but if the quantity of water absorbed exceeds that amount, the gunpowder will not burn off rapidly, and when dried the single grains become covered with an efflorescence of saltpetre, of course impairing the composition and active qualities of the powder. Even what is termed dry powder contains at least 2 per cent. of hygroscopic moisture. Powder can be exploded by a heavy blow as well as by an increase of temperature, and as regards its explosion by a blow, very much depends upon the material upon which it is placed and with which the blow is imparted. The following list exhibits in decreasing order the materials between which a blow most readily ignites powder:—Iron and iron, iron and brass, brass and brass, lead and lead, lead and wood, copper and copper, copper and bronze. For this reason gunpowder magazines are provided with doors turning upon bronze and copper hinges, the locks also being of copper. When dry powder is rapidly heated to above 300° it explodes. Even if only a very small portion of the powder is thus rapidly elevated in temperature, the entire quantity, be it large or small, is exploded; hence, a very small quantity touched by a red-hot or burning body is sufficient to effect an explosion. It is generally held that the charcoal is first ignited, and that it spreads the ignition to the other materials. Although Mr. Hearder found by experiment that powder does not ignite when touched with a red-hot platinum wire while under the receiver of an air-pump, Professors v. Schrötter and Abel proved that gunpowder so placed ignited rapidly when heated by a spirit-lamp.

Composition of Gunpowder. Gunpowder consists very nearly of 2 molecules of saltpetre, 1 molecule of sulphur, and 3 of charcoal. Accordingly 100 parts of powder contain—

Saltpetre	74·84
Sulphur	11·84
Charcoal (No. I.)	13·32

The above figures approximately express the composition of the best kinds of sporting and rifle-powder. Ordinary powders, such as blasting-powder, consist of nearly equal molecules of nitrate of potassa and sulphur, with 6 molecules of charcoal. Accordingly 100 parts contain—

Saltpetre	66·03
Sulphur	10·45
Charcoal (No. II.)	23·52

Products of the Combustion of Powder.

Drs. Bunsen and Schischkoff found the composition of a sporting and rifle-powder to be, in 100 parts, as follows:—

	Saltpetre	78·99
	Sulphur	9·84
Charcoal consisting of	Carbon	7·69
	Hydrogen	0·41
	Oxygen	3·07
	Ash	traces

The residue of this powder after combustion was found to consist of—

Sulphate of potassa	56·62
Carbonate of potassa	27·02
Hyposulphite of potassa	7·57
Sulphuret of potassium	1·06
Hydrated oxide of potassa (caustic potassa)	1·26
Sulphocyanide of potassium	0·86
Saltpetre	5·19
Carbon	0·97
Carbonate of ammonia Sulphur	traces
	100·55

It appears from this analysis that the residue left after ignition of the gunpowder consists essentially of sulphate and carbonate of potassa, and not, as has been formerly stated, of sulphuret of potassium. The composition of the smoke of the powder was ascertained to be—

Sulphate of potassa	65·29
Carbonate of potassa	23·48
Hyposulphite of potassa	4·90
Sulphuret of potassium	—
Caustic potassa	1·33
Sulphocyanide of potassium	0·55
Saltpetre	3·48
Carbon (charcoal)	1·86
Sesquicarbonate of ammonia	0·11
Sulphur	—
	100·00

From these figures it is clear that the smoke of gunpowder consists essentially of the same substances as the residue from the combustion, the only difference being that the sulphur and nitrate of potassa of the powder have been more completely converted into sulphate of potassa, while instead of the sulphuret of potassium, carbonate of ammonia makes its appearance. 100 parts by volume of the gaseous products of the combustion were found to consist of—

Carbonic acid	52·67
Nitrogen	41·12
Oxide of carbon	3·88
Hydrogen	1·21
Sulphuretted hydrogen	0·60
Oxygen	0·52
Protoxide of nitrogen	—
	100·00

The solid residues of combustion formed during the generation of the gases were found to be—

Sulphate of potassa	62·10
Carbonate of potassa	18·58
Hyposulphite of potassa	4·80
Sulphuret of potassium	3·13
Sulphocyanide of potassium	0·45
Nitrate of potassa	5·47
Charcoal	1·07
Sulphur	0·20
Sesquicarbonate of ammonia	4·20
	100·00

The decomposition of powder by its ignition may be represented by the following formulæ:—

$$1\text{ grm. of powder}\left\{\begin{array}{ll}\text{Saltpetre} & 0{\cdot}789\\ \text{Sulphur} & 0{\cdot}098\\ \text{Charcoal} & \left\{\begin{array}{l} \text{C } 0{\cdot}076\\ \text{H } 0{\cdot}004\\ \text{O } 0{\cdot}030\end{array}\right.\end{array}\right\}\begin{array}{c}\text{yields after}\\ \text{combustion}\end{array}\left\{\begin{array}{ll} \begin{array}{c}\text{Residue}\\ 0{\cdot}680\end{array} & \left\{\begin{array}{lr} & \text{Grm.}\\ K_2SO_4 & 0{\cdot}422\\ K_2CO_3 & 0{\cdot}126\\ K_2S_2O_3 & 0{\cdot}032\\ K_2S & 0{\cdot}021\\ KCNS & 0{\cdot}003\\ KNO_3 & 0{\cdot}037\\ C & 0{\cdot}007\\ S & 0{\cdot}001\\ (NH_4)_2CO_3 & 0{\cdot}028\end{array}\right.\\ \begin{array}{c}\text{Gases}\\ 0{\cdot}314\\ \hline 0{\cdot}994\end{array} & \left\{\begin{array}{lrcr} & \text{Grm.} & & \text{C.c.}\\ N & 0{\cdot}0990 & = & 79{\cdot}40\\ CO_2 & 0{\cdot}2010 & = & 101{\cdot}71\\ CO & 0{\cdot}0090 & = & 7{\cdot}49\\ H & 0{\cdot}0002 & = & 2{\cdot}34\\ SH_2 & 0{\cdot}0018 & = & 1{\cdot}16\\ O & 0{\cdot}0014 & = & 1{\cdot}00\\ \hline & & & 193{\cdot}10\end{array}\right.\end{array}\right.$$

According to the recent researches of Mr. Craig, and later investigations of M. Fedorow (1869), the products of the combustion of powder vary according to the pressure this substance is subjected to while being ignited. There has not hitherto been found any really effective substitute for gunpowder; fulminates and mixtures containing chlorate of potassa ignite too quickly and cause the bursting of the gun, while gun-cotton yields among its products of ignition water and nitrous acid, which act destructively on the metal, and also interfere with continued firing.

New kinds of Blasting Powder. Under the name of pyronene there is sold a new kind of blasting-powder, consisting of nitrate of soda 52·5 parts, sulphur 20, and spent tan 27·5 parts. It is, of course, far cheaper than ordinary powder, but presumably not very useful nor active. Captain Wynands, of Belgium, has successfully introduced a substance, to which he has given the name saxifragine, consisting of nitrate of baryta 76, charcoal 22, and nitrate of potassa 2 parts. Schultze's (1864) wood-gunpowder consists of granulated wood treated with a mixture of nitric and sulphuric acids, and next impregnated with a solution of nitrate of potassa; this material is manufactured at Edgeworth Lodge, Hants. M. Bändisch has invented a process by which this wood-gunpowder may be compressed into a solid substance exerting great power, and free from danger by transport. Lithofracteur, a white blasting-powder used in Belgium, is a substance similar to gun-cotton. The haloxylin of MM. Neumeyer and Fehleisen is a mixture of charcoal, nitre, and yellow prussiate of potassa. Callou's blasting powder is a mixture of chlorate of potassa and orpiment. Nitroleum is, in fact, nitroglycerine, which, with dynamite and dualin, will be spoken of presently. Picrate of potassa is used in France and in England for filling shells intended for the destruction of armour-plated ships, and for the manufacture of picrate gunpowder.

Testing the Strength of Gunpowder. In order to determine the strength or projectile force of gunpowder, and which for equality of composition is dependent on the mechanical treatment the powder has undergone, the following apparatus are used:—Test mortar, rod testing machine, lever testing machine, ballistic pendulum, and chronoscope. The first of these contrivances is a piece of heavy ordnance, charged with 92 grms. of powder, and a ball weighing 29·4 kilos., the mortar being placed at an angle of 45°. The bore of the mortar is 191 millemetres in diameter by 239 in depth. Powder of good quality should propel the ball a distance of 225 metres, and frequently the ball is carried a distance of 250 to 260 metres. The rod gunpowder testing apparatus consists of a mortar placed vertically, and which, when charged with 22 to 25 grms. of powder, lifts a weight of 8 lbs., made to move between toothed rods; by the height this weight is raised, springs attached to the weight fastening in the notches of the rods and holding it, the quality of the powder is judged.

White Gunpowder. In the year 1849 M. Augendre brought out a new kind of gunpowder, which, under the names of German white and American white gunpowder, has been occasionally employed. This powder consists of yellow prussiate of potassa, chlorate of potassa, and cane sugar. These materials, having been thoroughly mixed in a dry state, can be used in powder or in grains, igniting in contact with red-hot and flaming substances, but not by friction nor percussion. This white gunpowder may be preferred to the ordinary powder for the following reasons:—Being composed of unvarying substances, this powder can always, by weighing out the proper quantities of each ingredient, be obtained of uniform strength and quality. The ingredients are not hygroscopic to any extent, and are not acted upon by exposure to the air. The manufacture requires but a very short time, the projectile force is far greater, and the powder need not be granulated. On the other hand, this powder acts, during its ignition, so very strongly upon iron and steel that it can only be used in bronze ordnance, and in the filling of shells, &c. It is more readily fired than ordinary gunpowder, although less so than other mixtures containing chlorate of potassa. Finally, its manufacture is very expensive. According to the experiments of J. J. Pohl (1861) on this subject, the following is the best recipe for this powder:—

Yellow prussiate of potassa	28 parts
Loaf Sugar	23 „
Chlorate of potassa..	49 „

This mixture is approximatively equal to—

1 molecule of Prussiate of potassa,
1 „ Sugar,
3 molecules of Chlorate of potassa;

corresponding in 100 parts to 28·17 of prussiate of potassa, 22·78 of sugar, and 49·05 of chlorate of potassa. As no accurate and reliable analyses of the products of the combustion of this powder have been made, and as these products will vary with respect to the conditions under which the ignition takes place, whether in open air or in a close vessel, it can be merely calculated, that assuming complete combustion to take place, 100 parts of this powder will yield:—

Nitrogen..	1·865 parts
Carbonic oxide	11·192 „
Carbonic acid	17·587 „
Water	16·788 „
Total gaseous products ..	47·442 „

The solid residue will consist of—

Cyanide of potassium ..	17·385 parts
Chloride of potassium ..	29·840 „
Carburet of iron (FeC_2)	5·333 „
Total non-volatile products	52·558 „

The bulk of gaseous matter evolved by the ignition of 100 grms. of this powder, taken at 0° and 760 m.m. Bar., is as follows:—

Nitrogen.. ..	1927·0 cubic centims.
Carbonic oxide	8942·9 „
Carbonic acid	8942·9 „
Aqueous vapour	20867·9 „
	40680·4 „

As the temperature of combustion is estimated at 2604·5° the quantity of the gases is 431162 c.c.

Chemical Principles of Pyrotechny. Under the name of fireworks we include certain mixtures of combustible substances employed as signals, as destructive agents (for instance, Congreve rockets), and for purposes of display.

The various forms are, according to the end in view, so contrived as to burn off either rapidly or slowly, and with more or less emission of gaseous matter, heat, and light. These mixtures are mainly distinguished as heat-producing, ignition communicators (technically termed a match), and light-producing. The principle of the rational manufacture of fireworks, applying the word in its extended sense, is that neither any excess of the combustible nor of the combustion promoting and supporting agents should be employed, and that unavoidable accessory materials, viz., such as are intended only to keep the essential ingredients in a certain required shape, the paper casings, &c., be in precisely the quantity required. The best proportions of the combustible and combustion-supporting substances can be readily ascertained by theoretical calculations; for instance, it will be evident that a mixture of 2 equivalents of saltpetre and 1 equivalent of sulphur (1), or a mixture of 2 equivalents of saltpetre and 3 equivalents of sulphur (2), is in each instance wrong; in the latter, too much of the combustible body is used; and in the former case, too much of the supporter of combustion is employed:—

(1). S can take up from $2KNO_3$ at most $3O$, consequently $3O$ remain inactive.

(2). $3S$ and $2KNO_3$ yield either K_2S and $2SO_3$, or a mixture of K_2SO_4, K_2S, and SO_2; in each case some sulphur remaining unburnt.

We have to bear in mind, however, that it is not always possible to elucidate theoretically the decomposition of firework mixtures, as the affinity of the substances which react upon each other is not well known, and depends on accessory conditions and comparatively unknown influences. It will require a more advanced knowledge of the products of the decomposition of the different substances and their specific heat before we can predict with some degree of certainty the best mixtures. As regards the existing mixtures, they are the result of a lengthy series of experiments, really made by rule of thumb, though with a certain correspondence with the best composition theory can give, that is to say, many of these mixtures have been somewhat modified and improved by modern science.

The more commonly used Firework Mixtures. These mixtures consist mainly of saltpetre, sulphur, and charcoal, either in the same proportions as those in use for gunpowder, or with an excess of sulphur and charcoal. Some mixtures contain instead of saltpetre chlorate of potassa and other salts, not always essential to the combustion, but intended either to intensify the light evolved or impart to it a distinctive colour, as in signals and Bengal lights.

Gunpowder Is used in fireworks when it is desired that there should be projectile force. A slower combustion of the powder is obtained partly by the use of the so-called flour of powder, that is pulverised, not granulated powder, partly by compressing the mixture. If, however, it is intended to produce loud reports, granulated powder is used.

Saltpetre and Sulphur Mixture. This consists of 2 molecules (75 parts by weight) of saltpetre, and 1 molecule (25 parts by weight) of sulphur, and is used as the chief constituent of such firework mixtures as are intended to burn off slowly and evolve a strong light. However, this mixture is not used by itself for two reasons, viz., it does not develope a sufficient degree of heat to support its continued combustion, and does not possess a sufficient projectile force, being capable of producing in the best possible condition of complete ignition only 1 molecule of sulphurous acid—

$$2KNO_3 + S = K_2SO_4 + SO_2 + N;$$

that is to say, 1 part by bulk of this mixture only yields 7·28 volumes of gas. For these reasons the saltpetre-sulphur mixture is employed with charcoal or floury gunpowder.

Grey-coloured Mixture. Such a mixture, sanctioned by long use, is that known as grey-coloured mixture, consisting of 93·46 per cent. of saltpetre-sulphur, and 6·54 of floury gunpowder. This mixture is the chief constituent of other compounds intended to burn slowly, emitting at the same time a brilliant light, owing to the fact that the sulphate of potassa formed by the combustion acts similarly to a solid brought to an incandescent state. All mixtures intended to emit light, including coloured lights, are prepared upon the same principle, that the salt which is to give colour shall be non-volatile at the temperature of combustion.

Chlorate of Potassa Mixtures. This salt, $KClO_3$, when in presence of combustible substances, gives off its oxygen to the latter more readily, rapidly, and completely than saltpetre; accordingly this salt is used in all mixtures in which it is desired to combine rapid ignition with combustion. Formerly a mixture of 80 parts by weight of chlorate of potassa and 20 parts of sulphur, was added to intensify and quicken the combustion of mixtures consisting of more slowly burning salts. **Friction Mixtures. Percussion Powders.** A mixture of sulphur, charcoal, and chlorate of potassa constitutes an active percussion powder. A mixture of equal parts by weight of black sulphuret of antimony and chlorate of potassa is used for the purpose of discharging ordnance by means of a percussion tube placed into the touchhole of the gun. Sir William Armstrong uses for this purpose a mixture of amorphous phosphorus and chlorate of potassa.

Mixture for Igniting the Cartridges of Needle-guns. This mixture consists either of chlorate of potassa and black sulphuret of antimony, or a compound containing fulminate of mercury. The following is a good preparation:—16 parts of chlorate of potassa, 8 parts of black sulphuret of antimony, 4 of flour of sulphur, 1 of charcoal powder, are moistened with either gum or sugar water, and about 5 drops of nitric acid added. A small quantity, technically known as the *pill*, is placed in the cartridge, and ignited by the friction produced by the sudden passage of the steel needle through it. In this country either the above or a mixture of amorphous phosphorus and chlorate of potassa is used. Leaving the fulminates of silver and mercury out of the question, the explosive bodies and their applicability to warlike purposes and war pyrotechny have not been sufficiently investigated. Nitromannite or fulminating mannite, the picrates of the alkalies, and nitroglycerine, of which we shall presently treat more fully, especially deserve notice. M. Dessignolles, who suggests that instead of saltpetre, picrate of potassa should be used in the manufacture of gunpowder, states that quite different products are formed by the ignition of picrate of potassa, when effected in the open air (*α*), or under pressure (*β*):—

$$\alpha.\ \underbrace{2C_6H_2K(NO_2)_3O}_{\text{Picrate of potassa.}} = K_2CO_3 + 5C + 2N + NO + NO_2 + 4CO_2 + CHN.$$

$$\beta.\ \underbrace{2C_6H_2K(NO_2)_3O}_{\text{Picrate of potassa.}} = K_2CO_3 + 6C + 3N + 5CO_2 + 2H_2 + O.$$

Fulminating aniline, chromate of diazobenzol, obtained by the action of nitrous acid upon aniline, and the precipitation of the product by the aid of a hydrochloric acid solution of bichromate of potassa, is, according to MM. Caro and Griess, an efficient substitute for fulminating mercury.

Heat-producing Mixtures. These consist chiefly of floury gunpowder and grey mixture, to which are added those organic substances, as pitch, resin, tar, igniting readily, but consumed more slowly than any firework. The heat generated by the combustion of fireworks is much higher than is required to ignite wood, but not of sufficient duration to cause the thorough burning of the wood, hence the addition of tar, &c.

Coloured Fires. The salts employed to produce coloured flames are—the nitrates of baryta, strontia, and soda, and the ammoniacal sulphate of copper. The so-called cold fused mixture, composed of grey mixture, floury gunpowder, and sulphuret of antimony, moistened with brandy and then mixed, produces a white flame. The mixtures for coloured fires used in artillery laboratories are the undermentioned, calculated for 100 parts of each mixture:—

	a. Green.	*b.* Red.	*c.* Yellow.	*d.* Blue.	*e.* White
1. Chlorate of potassa	32·7	29·7	—	54·5	—
2. Sulphur	9·8	17·2	23·6	—	20
3. Charcoal	5·2	1·7	3·8	18·1	—
4. Nitrate of baryta	52·3	—	—	—	—
5. Nitrate of strontia	—	45·7	—	—	—
6. Nitrate of soda	—	—	9·8	—	—
7. Ammoniacal sulphate of copper	—	—	—	27·4	—
8. Saltpetre	—	—	62·8	—	60
9. Black sulphuret of antimony	—	5·7	—	—	5
10. Floury gunpowder	—	—	—	—	15

It is hardly necessary to mention that great care is required in mixing these materials, and that each ingredient ought to be pulverised separately.

According to M. Uhden a beautiful white flame edged with blue is obtained by the ignition of the following mixture:—20 parts of saltpetre, 5 of sulphur, 4 of sulphuret of cadmium, and 1 part of charcoal. Chloride of thallium with other ingredients yields a beautiful green flame. Magnesium was used during the Abyssinian war in various ways when a brilliant light was required. The chlorates of the alkaline earth bases and the chlorate of soda would be preferable, were it not for the expense, and for the facts that these salts are rather hygroscopic and liable to spontaneous combustion. The carbonates of baryta and of strontia are sometimes used instead of the nitrate. According to MM. Dessignolles and Castelhaz, most brilliant coloured flames are obtained with picrate of ammonia in the following proportions:—

Yellow	Picrate of ammonia	50
	Picrate of protoxide of iron	50
Green	Picrate of ammonia	48
	Nitrate of baryta	52
Red	Picrate of ammonia	54
	Nitrate of strontia	46

b. *Nitroglycerine.*

Nitroglycerine. This substance, also known as fulminating oil, nitroleum, trinitrine, glyceryl-nitrate, glonoine, was discovered in 1847 by Dr. A. Sobrero, while a student in the laboratory of Professor Pelouze, at Paris. Since the year 1862, M. Alfred Nobel, a Swede, has manufactured this liquid on the large scale. The formula of nitroglycerine is $C_3H_5N_3O_9$ or $\left.\begin{matrix}C_3H_5\\(NO_2)_3\end{matrix}\right\}O_3$; consequently it consists of glycerine, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$, in which 3 atoms of H have been replaced by 3 atoms of NO_2. 100 parts of nitroglycerine yield on combustion—

Water	20 parts.
Carbonic acid	58 ,,
Oxygen	3·5 ,,
Nitrogen	18·5 ,,
	100·0 parts.

As the sp. gr. of nitroglycerine is 1·6, 1 part by bulk will yield on combustion—

Aqueous vapour	554 volumes.
Carbonic acid	469 ,,
Oxygen	39 ,,
Nitrogen	236 ,,
	1298 ,,

According to experiments made in Belgium, the combustion of nitroglycerine does not yield free oxygen, but a large quantity of protoxide of nitrogen; accordingly, the following equation will give some idea of the mode of explosion:—

$$\left.\begin{matrix}\text{2 molecules of}\\ \text{Nitroglycerine, } C_3H_5N_3O_9\end{matrix}\right\} = \left\{\begin{matrix}\text{Carbonic acid, } 6CO_2.\\ \text{Water, } 5H_2O\\ \text{Protoxide of Nitrogen, } N_2O.\\ \text{Nitrogen, } 4N.\end{matrix}\right.$$

M. Nobel states that the heat set free by explosion causes the gases to expand to eight times their bulk; accordingly, 1 volume of nitroglycerine will yield 10·384 volumes of gas, while 1 part by bulk of powder only yields 800 volumes of gas; the explosive force of nitro-glycerine is, therefore, to that of powder—

By volume as 13 : 1,
By weight as 8 : 1.

In order to prepare nitroglycerine, very strong nitric acid, density 49° to 50° B. = 1·476 to 1·49 sp. gr., is mixed with twice its weight of concentrated sulphuric acid. 3300 grms. of this mixture, thoroughly cooled, are poured either into a glass flask or into a glazed earthenware jar, placed in a pan of cold water, and there is next gradually added 500 grms. of concentrated and purified glycerine, having a density at least of 30° to 31° B. = sp. gr. 1·246 to 1·256, care being taken to stir constantly According to Dr. E. Kopp's recipe (1868) the acid mixture should consist of 3 parts of sulphuric acid at 66° B. = 1767 sp. gr., and 1 part of fuming nitric acid. To 350 grms. of glycerine 2800 grms. of the acid mixture are added; and in performing this operation care should be taken to avoid any perceptible heating for fear of converting by a violent reaction the glycerine into oxalic acid. The mixture is now left to stand for five or ten minutes, and afterwards poured into five or six times its bulk of very cold water, to which a rotatory motion has been imparted. The newly-formed nitroglycerine sinks to the bottom of the vessel as a heavy oily liquid, which is washed by decantation; but if not intended for transport—and experience has proved the transport of nitroglycerine to be highly dangerous—the washing may be dispensed with, as neither any adhering acid nor water impairs the explosive properties. Nitroglycerine is now generally made on the spot in America and elsewhere by those whom experience in mining, quarrying, and engineering matters has taught the real value of this very powerful agent.

Nitroglycerine is an oily fluid of a yellow or brown colour, heavier than and insoluble in water, soluble in alcohol, ether, and other fluids; when exposed to continuous cold, not of great intensity, it becomes solidified, forming long needle-shaped crystals. The best means of exploding nitroglycerine is a well-directed blow, neither a spark nor a lighted body will cause the ignition, which even with a thin layer takes place with difficulty, only part being consumed. A glass bottle filled with nitroglycerine may be smashed to pieces without causing the contents to explode. Nitroglycerine may even be gently heated and volatilised without decomposition or combustion, provided violent boiling is carefully prevented. When a drop of nitroglycerine is caused to fall on a moderately hot piece of cast-iron the liquid is quietly volatilised; if the iron is red-hot the liquid burns off instantaneously, just as a grain of powder would do under the same conditions; if, however, the iron is at that heat which will cause the immediate boiling of the nitroglycerine, it explodes with great force. Nitroglycerine, especially if sour and impure, is liable to spontaneous decomposition, which, accompanied by the formation of gas and of oxalic acid, may have been the proximate cause of some of the dreadful explosions of this substance, it being surmised that the pressure exerted by the generated gases upon the fluid in hermetically closed vessels had something to do with the occurrences. On this account M. K. List advises that vessels containing nitroglycerine should be only loosely stoppered, or if being transported provided with safety-valves. Nobel secures nitroglycerine from explosion by dissolving it in pure wood-spirit, from which it may be again separated by the addition of a large quantity of water. Mr. Seeley on this score observes that:—1. The wood-spirit is expensive, and lost in the large quantity of water required for precipitating the nitroglycerine; 2. Wood-spirit, being volatile, may evaporate, and leave the nitroglycerine unprotected; 3. There is a change of chemical action between these bodies; 4. The vapour of wood-spirit is very volatile, and forms with air an explosive mixture. Many suggestions have been made as to rendering nitroglycerine safe to warehouse; among them may be noted the mixing with pulverised glass in a manner similar to Gale's process for gunpowder. Wurtz recommends the mixture of nitroglycerine with equally dense solutions of either of the nitrates of zinc, lime, or magnesia, so as to form an emulsion, the nitroglycerine being recovered simply by the addition of water. The taste of nitroglycerine is sweet, but at the same time burning and aromatic; it is a violent poison even in small doses, and its vapour is of course equally virulent, hence great care is required in working with this substance in localities where, as in mines and pits, the supply of fresh air is limited. Instead of manufacturing nitroglycerine in works specially arranged for that purpose, and transporting this dangerous compound, it is better, as advised by and executed under the direction of Dr. E. Kopp, at the Saverne quarries, to have the quantity required for daily use prepared on the spot by intelligent workmen. Notwithstanding the very serious accidents which have been caused by the explosions of nitroglycerine in this country as well as abroad, and the consequent prohibition of its use, there is no reason why this powerful agent should not be employed according to Kopp's suggestion. Instead of the acid mixture used in the preparation of nitroglycerine, M. Nobel suggests the following:—In 3½ parts of strong sulphuric acid of 1·83 sp. gr. is dissolved 1 part of saltpetre, and the fluid cooled down; the result is the separation of a salt consisting of 1 molecule of potassa, 4 molecules of sulphuric acid, and 6 molecules of water, and which at 32° F. is altogether eliminated from the fluid, leaving an acid which, by the gradual addition of glycerine, is converted into glonoine, afterwards separated by water, as already described.

Nobel's Dynamite. Under the name of dynamite, Nobel, in 1867, brought out a new explosive compound, consisting of 75 parts of nitroglycerine absorbed by 25 parts of any porous inert matter, as finely-divided charcoal, silica. As evidenced by the experiments of Bolley and Kundt, dynamite has the advantage over nitroglycerine of not being exploded even by the most violent percussion, therefore requiring a peculiarly-arranged cartridge. The explosion is attended with such force that large blocks of ice are shattered to atoms. Dynamite burns off quietly in open air, or even when loosely packed, the combustion being accompanied by an evolution of some nitrous acid; but when dynamite is exploded there are generated only carbonic acid, nitrogen, and aqueous vapour, no smoke being formed, and only a white ash left. Dynamite is not affected by damp, and undoubtedly offers great advantages as regards its use in mining, quarrying, and similar operations, for although the price exceeds four times that of powder, dynamite performs eight times as much work with less danger, and less labour in boring blast holes. The dynamite is placed in cartridges of thick paper, and ignited by means of a fusee, which passes through the sand serving the purpose of a wad. Dynamite can be transported without danger of explosion. Dittmar's dualin is a mixture of nitroglycerine with saw-dust or wood-pulp as used in paper mills, both previously treated with nitric and sulphuric acids.

c. *Gun-Cotton.*

Gun-Cotton. This substance, also known as pyroxylin and fulmicotton, was discovered in 1846, simultaneously by the late Professor Schönbein, at Balse, and by Dr. R. Böttger, at Frankfort-on-Main. The mode of preparing this substance is as follows:—Equal parts of strong concentrated sulphuric acid, sp. gr. = 1·84, and fuming nitric acid are poured into a porcelain basin; as much cotton-wool is steeped in the fluid as the acid is capable of thoroughly moistening, and the vessel covered with a glass plate, and left for a few minutes. The cotton-wool is then removed from the acid, immediately transferred to a vessel containing a large quantity of water, and washed with care, the water being renewed until no more acid adheres to the gun-cotton, which is next dried in a current of warm air, and finally combed to remove all the lumps. The cotton should not be left too long in the acid, as it might become entirely dissolved. According to experiments instituted at Paris, in one of the powder mills—for in France no one is allowed to manufacture powder or gun-cotton except the Government—the following are the conditions under which the best results are obtained:—1. Equal parts of sulphuric and nitric acids and well-cleansed cotton. 2. Time of immersion in acid mixture from 10 to 15 minutes. 3. The same acid may be used once again, but then the time of immersion of the cotton should be longer. 4. The gun-cotton having been thoroughly washed should be dried slowly at a gentle heat. 5. Impregnating with nitre increases the strength of the gun-cotton.

Properties of Gun-Cotton. In its outward appearance gun-cotton does not differ from ordinary cotton, neither is any difference perceptible by microscopic investigation. It is insoluble in water, alcohol, and acetic acid, difficultly soluble in pure ether, but readily soluble in ether which contains alcohol, and in acetic ether. Gun-cotton is liable to spontaneous decomposition, which may even induce its spontaneous combustion; this decomposition is attended with the evolution of aqueous vapour and of nitrous acid fumes, the remaining substance containing formic acid. As regards the temperature at which gun-cotton ignites statements differ; it has in some instances been dried at 90° to 100° without any dangerous consequences, while it has been found to ignite at 43°. Instances are on record of serious explosions of gun-cotton having taken place under conditions which leave no doubt that the greatest care is required in handling and warehousing this substance; for instance, a small magazine, filled with gun-cotton, situated in the Bois de Vincennes, Paris, was exploded by the sun's rays; and at Faversham the Le Bouchet drying-rooms, which could not possibly be heated above 45° to 50°, exploded with great violence. Gun-cotton explodes by percussion, leaving no residue after its ignition. Good gun-cotton may be burned off when placed on dry gunpowder without igniting the latter. It is very hygroscopic, but may be kept for a length of time under water without affecting its explosive properties.

According to the best chemical analysis, gun-cotton is trinitro-cellulose,

$$C_6H_7(NO_2)_3O_5,$$

consequently it is cotton considered in a pure state as cellulose, $C_6H_{10}O_5$, 3 atoms of the hydrogen of which have been replaced by 3 atoms of hyponitric acid. 100 parts of gun-cotton contain—

Carbon	24·24
Hydrogen	2·36
Oxygen	59·26
Nitrogen	14·14
	100·00

The conversion of cotton into gun-cotton may therefore be expressed by the following formula:—

$$\underbrace{C_6H_{10}O_5}_{\text{Cotton.}} + 3HNO_3 = \underbrace{C_6H_7(NO_2)_3O_5}_{\text{Gun-Cotton.}} + 3H_2O\,;$$

the sulphuric acid being employed only for the purpose of absorbing water. Assuming that the cellulose is entirely converted into trinitro-cellulose, 100 parts of cotton ought to yield 185 parts of gun-cotton, and when the conversion forms binitro-cellulose, 100 parts of cotton ought to yield 155 parts of gun-cotton. The under-mentioned are the results of direct investigation. For 100 parts of cotton—

Pelouse (in ten experiments, 1849)	found 168 to 170	parts of	gun-cotton.
Schmidt and Hecker (1848)	,, 169	,,	,,
Van Kerckhoff and Reuter (1849)	,, 176·2	,,	,,
W. Crum (1850)	,, 178	,,	,,
Redtenbacher, Schrotter, and Schneider (1864)	,, 178	,,	,,
V. Lenk (1862)	,, 155	,,	,,
Blondeau (1865)	,, 165·25	,,	,,

By the explosion of gun-cotton *in vacuo*, carbonic oxide, aqueous vapour, and nitrogen are evolved. The same products, with the addition of nitrous acid and cyanogen, are generated by the explosion of gun-cotton in closed vessels. 1 grm. of gun-cotton yields, according to Schmidt, 588 c.c. gases, these gases consisting in 100 parts by volume of—

Carbonic oxide	30
Carbonic acid	20
Marsh gas	10
Deutoxide of nitrogen	9
Nitrogen	8
Aqueous vapour	23
	100

1 part by weight of gun-cotton is equal in projectile power to 4·5 to 5 parts of gunpowder.

Gun-Cotton as a Substitute for Gunpowder. Gun-cotton has not yet been adopted in practice as a good substitute for gunpowder; its large bulk, coupled with the fact that the explosion is attended with the evolution of much water and nitrous acid, render it inconvenient as a substitute for powder.

Other uses of Gun-Cotton. Gun-cotton is advantageously employed in blasting, and has been used as a substitute for fulminating mercury in gun-caps when mixed with chlorate of potassa. The experiments of Professor Abel, of Woolwich, have led to great improvements in the manufacture of gun-cotton, carried into practice by Messrs. Prentice, of Stowmarket, and consisting chiefly in mechanical operations. The cotton, either by spinning and weaving, by pulping, or the aid of suitable solvents, is brought into a condition in which it has been found an excellent and cleanly substitute for gunpowder, having the advantages of not giving off smoke, exploding with less noise, and not fouling the guns. The detailed description of the method of these operations is not necessary here. Gun-cotton in many cases may serve the purpose of asbestos for filtering strong acids and other concentrated fluids which cannot be filtered through paper.

Collodion. Maynard employs a solution of gun-cotton in ether as a kind of glue or varnish, and gives it the name of collodion. This solution has the appearance of a syrup, and a thin film poured on the skin, leaves, by the evaporation of the ether, a strongly adhesive compact layer; hence collodion is applied in surgery, photography, and as a waterproof coating instead of varnish, especially to protect the composition of lucifer-matches from the effects of damp. The film of pyroxylin, deposited after the evaporation of ether, is insoluble in water and alcohol, becomes highly negatively electric when rubbed with the dry hand, and may be obtained so thin as to exhibit the colours of the Newton rings. Legray prepares in the following manner a gun-cotton quite soluble in ether:—80 grms. of dried and pulverised nitrate of potassa are mixed with 120 grms. of concentrated sulphuric acid, and in the pulpy acid mass are thoroughly immersed by the aid of a glass rod or porcelain spatula 4 grms. of cotton, which is stirred about for a few minutes; next the vessel containing acid and cotton is placed in a large quantity of water, and the converted cotton washed until all the acid is eliminated, when it is dried. Soluble cotton may be made with nitrate of soda, 17 parts; sulphuric acid, sp. gr. = 1·80, 33 parts; cotton, ½ part. The converted cotton is soluble in acetic ether, acetate of oxide of methyl, wood-spirit, and aceton; the usual solvent is a mixture of 18 parts of ether and 3 parts of alcohol.

COMMON SALT.

Occurrence. Common salt, or chloride of sodium, consists of—

Chlorine, Cl	35·5	60·41
Sodium, Na	23·0	39·59
	58·5	100·00

and is found on our globe in the solid, as rock-salt, as well as dissolved in sea-water in enormously large quantities. It occurs as rock-salt in extensive layers alternating with those of clay and gypsum at an average depth of 100 metres. The following are a few of the localities where rock-salt is met with in the tertiary formation:—Wieliczka, Poland; the northern slopes of the Carpathian mountains, and in several districts of Hungary; in the chalk formation of Cardona, Spain; in the Eastern Alps, Bavaria, Salzburg, Styria, and the Tyrol. Among the trias formation are the salt deposits of the Teutoburg-wood, Germany, and a great many others, among them the celebrated Stassfurt deposits. In England rock-salt is found in Cheshire, this county being also plentifully supplied with saline springs, the water of which yields on evaporation an abundance of salt. Petroleum wells are found with salt in many parts of Asiatic Russia, in Syria, Persia, and the slopes of the Himalaya. Salt occurs plentifully in several districts of Africa, America, and other parts of the world, and mixed with clay and marl, forming salt-clay. Salt occurs secondarily by having been dissolved, at a depth varying in Germany from 91 to 555 metres, by water, which carries it again to the surface, there forming salt springs and salt lakes, from which the salt is obtained by evaporation. Among the salt lakes may be noticed the lake near Eisleben, Germany, the Elton Lake, near the Wolga, Russia, the Dead Sea, and the Salt Lake of Utah, United States.

There can be no doubt that the common salt met with in salt springs owes its origin to the solvent action of water upon rock-salt, and as rock-salt is largely met with in sedimentary geological formations, the prevalence of this formation in Germany has there given rise to a large number of salt springs. Common salt is also found in sea-water, and if obtained by its evaporation is often termed sea-salt; or if deposited, as is the case in the Polar regions, by intense cold on the surface of ice-fields, it is known as *rassol*. Common salt is largely obtained as a by-product of some chemical operations, as in the conversion of sodium-nitrate into potassium-nitrate by the aid of chloride of potassium.

Method of Preparing Common Salt from Sea-Water. The constituent salts of sea-water do not differ in any part of the world: even the difference in quantity is very small, and is generally due to local causes, as the dilution of the sea-water by river-water, melting icebergs, &c. The sp. gr. of sea-water at 17°, varies from 1·0269 to 1·0289, the sp. gr. of the water of the Red Sea being as high as 1·0306. One hundred parts of sea-water contain—

	Pacific Ocean.	Atlantic Ocean.	German Ocean.	Red Sea.
Chloride of sodium	2·5877	2·7558	2·5513	3·030
Bromide of sodium	0·0401	0·0326	0·0373	0·064
Sulphate of potassa	0·1359	0·1715	0·1529	0·295
Sulphate of lime	0·1622	0·2046	0·1622	0·179
Sulphate of magnesia ..	0·1104	0·0614	0·0706	0·274
Chloride of magnesium ..	0·4345	0·3260	0·4641	0·404
Chloride of potassium ..	—	—	—	0·288
	3·4708	3·5519	3·4384	4·534

The composition of the salt contained in the water of the several seas is shown by the following table:—

	Caspian Sea.	Black Sea.	Baltic.*	English Channel. Average of 7 localities.	Mediterranean. Average of 2 localities.	Atlantic Ocean. Average of 3 localities.	Dead Sea. Average of 5 localities.
Average quantity of salt and water—							
Solid salt	0·63	1·77	1·77	3·31	3.37	3·63	22·30
Water	99·37	98·23	98·23	96·69	96·63	96·37	77·70
The dissolved solid matter consists in 100 parts of—							
Chloride of sodium ..	58·25	79·39	84·70	78·04	77·07	77·03	36·55
Chloride of potassium.	1·27	1·07	—	2·09	2·48	3·89	4·57
Chloride of calcium ..	—	—	—	0·20	—	—	11·38
Chloride of magnesium	10·00	7·38	9·73	8·81	8·76	7·86	45·20
Bromides of sodium and magnesium	—	0·03	—	0·28	0·49	1·30	0·85
Sulphate of lime . .	7·78	0·60	0·13	3·82	2·76	4·63	0·45
Sulphate of magnesia ..	19·68	8·32	4·96	6·58	8·34	5·29	—
Carbonates of lime and magnesia	3·02	3·21	0·48	0·18	0·10	—	—
Nitrogenous and bituminous matter	—	—	—	—	—	—	1·00

One cubic metre (35·3165 cubic feet) of sea-water contains consequently about 28 to 31 kilos. of chloride of sodium, and 5 to 6 kilos. of chloride of potassium. Chloride of sodium (common salt) is obtained from sea-water:—

a. By the evaporation of the water by the aid of the sun's heat.
b. In winter by freezing.
c. By artificial evaporation.

Method of Obtaining Common Salt in Salines.

This method of obtaining common salt from sea-water is limited to certain of the coast-lines of Southern Europe, and is never effected beyond 48° N. latitude. The countries best situated for this industry are France, Portugal, Spain, and the coasts of the Mediterranean. The arrangement of the salines, or salt-gardens, is the following:—On a level sea-shore is constructed a large reservoir, which, by a short canal, communicates with the sea, care being taken to afford protection against the inroads of high tides. The depth of water in these reservoirs varies from 0·3 metres to 2 metres. The sea-water is kept in the reservoir until the suspended matter has been deposited, and is then conveyed by a wooden channel into smaller reservoirs, from which it is conducted by underground pipes to ditches surrounding the salines, where the salt is separated from the water. The salt is collected, placed in heaps on the narrow strips of land which separate the ditches from each other, and sheltered from rain by a covering of straw. As these heaps are left for some time, the deliquescent chlorides of magnesium and calcium are absorbed in the soil, consequently the salt is comparatively pure. The mother-liquor is used in the production of chloride of potassium (see *ante*, p. 119), sulphate of soda, and magnesia salts, the process employed being that originally suggested by Professor Balard, and afterwards improved by Merle.

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* According to the experiments of Baron Sass, the water of the Baltic from the Great Sound between the Islands of Oesel and Moon only contains 0·666 per cent. of solid matter, and is of a sp. gr. = 1·00474.

By Freezing. This process is based upon the fact that when a solution of common salt is cooled to several degrees below the freezing-point, it is split up into pure water, which freezes, and a strong solution of salt. The solution becomes more concentrated by repeated freezing and removal of the ice, until at last a solution is obtained which by a slight evaporation yields a crop of salt. In order to render the product purer, some lime is added to the solution before evaporation to decompose the magnesia salts.

By Artificial Evaporation. Common salt evaporated from sea-water by the aid of fuel, or *sel ignifère*, is chiefly prepared in Normandy, in the following manner:—The sand impregnated with salt is employed to saturate the sea-water, which is next evaporated. Very frequently an embankment of sand is thrown up on the shore, so as to be covered at high tides only; in the interval between two tides a portion of the salt dries with the sand, which in hot summer weather is collected twice or three times daily. The sand is lixiviated in wooden boxes, the bottoms of which are constructed of loose planks covered with layers of straw; the sand having been put in the boxes sea-water is allowed to percolate through them till the specific gravity of the water increases to 1·14 or to 1·17, the density being observed by means of three wax balls weighted with lead. The salt boilers at Avrauchin consider that a solution or brine of 1·16 sp. gr. is the most suitable for evaporation. The evaporation is carried on in leaden pans, and during the process the scum is removed and fresh brine added until the salt begins to crystallise out, when again a small quantity of brine is added to produce more scum, which is at once removed, and the evaporation continued to dryness. The salt thus obtained, a finely divided but very impure material, is put into a conical basket suspended over the evaporating pan, the object being to remove by the action of the steam the deliquescent chlorides of calcium and magnesium. The salt is next transferred to a warehouse, the floor of which is constructed of dry, well-rammed, exhausted sand, and here it is gradually purified by the loss of deliquescent salts, the consequent decrease in weight amounting to 20 to 28 per cent. 700 to 890 litres of brine yield, according to the quantity of salt contained in the sand, 150 to 250 kilos. of salt. A very similar method is in use at Ulverstone, Lancashire.

At Lymington and the Isle of Wight, sea-water is concentrated by spontaneous evaporation to one-sixth of its original bulk, the brine being then evaporated by the aid of artificial heat. In the neighbourhood of Liverpool salt is obtained by employing sea-water in refining crude rock-salt; in this way at least 2·3 per cent. of common salt results as a by-product. During a continuation of hot summer weather, salt is deposited from the water of many of the salt lakes in immense quantities, amounting, for instance, at the Elton Lake, Russia, to 20 millions of kilos.

Rock-salt. This mineral is frequently accompanied by anhydrite, clay, and marl, and is sometimes found in what are termed pockets of irregular shape, interspersed with clay. Again, in some cases saline deposits are separated by layers of marl. With rock-salt other minerals sometimes occur, as, for instance, brongniartine $(Na_2SO_4 + CaSO_4)$, near Villarubia, in Spain, and the remarkable minerals of the salt deposit near Stassfurt. Above the latter deposit is a layer 65 metres thick, of bitter, many-coloured, deliquescent salts, consisting of 55 per cent. of carnallite, sylvin, and kainite; 25 per cent. of common salt; 16 per cent. of kieserite; and 4 per cent. of chloride of magnesium. As this saline layer contains 12 per cent. of potassa it is an important deposit in an industrial sense.

The composition of rock-salt is as follows:—

I. White rock-salt from Wieliczka; II. White, and III. Yellow rock-salt from Berchtesgaden; IV. From Hall in the Tyrol; V. Detonating salt from Hallstadt; VI. From Schwäbischhall.

	I.	II.	III.	IV.	V.	VI.
Chloride of sodium	100·00	99·85	99·92	99·43	98·14	99·63
Chloride of potassium	—	—	—	—	traces	0·09
Chloride of calcium	—	traces	—	0·25	—	0·28
Chloride of magnesium	traces	0·15	0·07	0·12	—	—
Sulphate of lime	—	—	—	0·20	1·86	—
	100·00	100·00	100·00	100·00	100·00	100·00

The so-called detonating salt, found at Wieliczka in crystalline granular masses, has the property when being dissolved in water of giving rise to slight detonations accompanied by an evolution of hydrocarbon gas from microscopically small cells, the walls of which becoming thin when the salt is dissolved in water, give way, and cause the report. If the solution of the salt takes place naturally in the mine, the gas partly escapes, partly becomes condensed, forming petroleum, often met with in beds of rock-salt. The minerals of the salt deposit of Stassfurt are, according to MM. Bischof, Reichardt, Zincke, and others, the following:—

	Chemical Formula.	In 100 parts are contained:	Sp. gr. of the compound.	100 parts of water dissolve at 18¾° C.	Synonyms and Observations.
Anhydrite..	$CaSO_4$	100 of Sulphate of lime	2·968	0·20	Karstenite.
Boracite ..	$B_{16}O_{30}Cl_2Mg_7$	26·82 Magnesia 65·57 Boric acid 10·61 Magnesium chloride	2·9	Almost insoluble	Stassfurtite.
Carnallite..	$KMgCl_3 + 6H_2O$	26·76 Chloride of potassium 34·50 Magnesium chloride 38·74 Water	1·618	64·5	Contains Bromine.
Red oxide of iron	Fe_2O_3	100 of Oxide of iron	3·35	Insoluble.	—
Kieserite ..	$MgSO_4 + H_2O$*	87·10 Sulphate of magnesia 12·90 Water	2·517	40·9	Martinsite?
Polyhalite. .	$2CaSO_4$ $MgSO_4$ K_2SO_4 $2H_2O$	45·18 Sulphate of lime 19·93 Sulphate of magnesia 28·90 Sulphate of potassa 5·99 Water	2·720	Is decomposed while being dissolved.	—

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* According to Rammelsberg it is probable that kieserite is originally an anhydrous mineral, a conclusion which seems justified by the variable quantity of water found in different analyses.

	Chemical formula.	In 100 parts are contained:	Sp. gr. of the compound.	100 parts of water dissolve at 18¾° C.	Synonyms and Observations.
Rock-salt ...	$NaCl$	100 Chloride of sodium	2·200	36·2	—
Sylvin ...	KCL	100 Chloride of potassium	2·025	34·5	—
Tachhydrite	$CaCl_2$ $2MgCl_2$ $12H_2O$	21·50 Chloride of calcium 36·98 Chloride of magnesium 41·52 Water	1·671	160·3	—
Kainite ...	K_2SO_4 $MgSO_4$ $MgCl_2$ $6H_2O$	36·34 Sulphate of potassa 25·24 Sulphate of magnesia 18·95 Magnesium chloride 19.47 Water	—	—	Contains Bromine.
Schönite or Pikromerite	K_2SO_4 $MgSO_4$ $6H_2O$	43·18 Sulphate of potassa 29·85 Sulphate of magnesia 26·97 Water.	—	—	—

Sylvin is also found in large quantities in the salt deposit near Kalucz, Galicia.

Mode of Working Rock-Salt. Rock-salt, like other minerals and according to its mode of occurrence, is either quarried or mined. If it happens, however, that the rock-salt is mixed with other minerals, clay, gypsum, dolomite, &c., a solution in water is effected, which is pumped up from the mine as a concentrated brine. In many instances rock-salt is wrought in extensive and deep mines, as in the celebrated rock-salt mines of Wieliczka.

Mode of Working Salt-springs. Natural salt-springs sometimes occur which have been imitated artificially by boring to a great depth into layers of earth containing saline deposits. In this manner a brine may be obtained sufficiently concentrated to be at once boiled down. The method of working the natural salt-springs is to form a convenient reservoir from which the saline solution is immediately pumped up for the purpose of being gradated (see p. 168). The solution previous to being boiled down is left to allow the suspended matter to settle. The salt-springs obtained by boring either yield a native brine, or the borings are carried into solid rock-salt and water caused to descend into the salt deposit. This artificial brine is then pumped up, unless there is naturally an artesian formation. The brine previous to further operations is left for some time in reservoirs to deposit suspended insoluble matter.[*]

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[*] These saline solutions are not always free from impurities; in considering their admixture brine may be divided into two classes; the first containing sulphate of magnesia or soda, with chloride of magnesium; the other class embraces brine containing the chlorides of calcium and magnesium. If the brine happens to pass through peaty soil or layers of lignite, there often accrues organic matter, humic, crenic, and apocrenic acids.

Preparation of Common Salt from Brine. This operation is duplex and consists in—

- *a.* Concentrating the brine.
  - *α.* By increasing the quantity of salt.
  - *β.* By decreasing the quantity of water.
- *b.* The boiling down of the concentrated brine.

Concentrating the Brine. Native brines or salt-springs seldom contain enough common salt to make it profitable to boil them down at once; it is consequently necessary to enrich the brine, and this may be done either (*α*) by dissolving in it rock-salt or crude sea-salt, neither being suited for culinary and many other purposes unless refined, or (*β*) by decreasing the quantity of water without the use of fuel.

Enriching by Gradation. The enriching or concentration of a brine by decreasing the quantity of water it contains is called a gradation process, and may be proceeded with by freezing off the water in winter time, or more generally by evaporating the water by a true gradation process; either—*a.* Gradation by the effect of the sun's rays. *b.* Table gradation. *c.* Roof gradation. *d.* Drop gradation.

Gradation by means of the sun's rays is obviously the same method of procedure as that described under the treatment of sea-salt. Table gradation has been only experimentally tried at Reichenhall, and consists simply in causing the brine to flow slowly from a reservoir down a series of steps, constructed so as to give as much surface as possible, and thus hasten the evaporation. Roof gradation is effected by utilising the roofs of the large tanks containing the brine as evaporation surfaces, by causing the contents of the tanks to flow in a thin but constant stream over the roofs, which, of course, are exposed to the open air.

Faggot Gradation. This operation, also known as drop gradation, is carried on by means of the following apparatus, termed gradation house, and consisting of a framework of timber, fitted with faggots of the wood of *Prunus spinosa*, which being thorny, presents a large surface. The entire construction is built over a water-tight wooden tank, which receives the concentrated brine, and frequently the top of the gradation house is provided with a roof. Under the roof and above the faggots a water-tight tank is placed containing the brine to be gradated; this tank is provided with a number of taps, from which the brine trickles into channels provided with holes to admit of the brine falling on the faggots. These taps are placed on both sides of the gradation house, and are generally connected with levers to admit of being readily turned on and off from below. The gradation process is continued until the brine is sufficiently concentrated to admit of being further evaporated by the aid of fuel; the brine may be gradated to contain 26 per cent. of salt, but the operation is rarely carried so far.

The gradation process not only serves the purpose of concentration, but also that of purifying the brine, as some of the foreign salts are deposited on the faggots, this deposit of course varying in composition according to the constituents of the brine, but chiefly consisting of carbonate of lime, with the sulphates of potassa, soda, and magnesia. The deposit has in some instances been used as manure. In the tanks where the gradated brine is collected another slimy deposit is gradually formed, consisting of gypsum and hydrated oxide of iron. As in the present day the brine obtained from bored wells is generally sufficiently concentrated to be at once boiled down, gradation is less frequent, being a very slow process and involving a loss of the salt carried off by the wind.

Boiling down the Brine. The object is to obtain with the least possible expenditure of fuel the largest quantity of pure dry salt. Formerly the evaporation was carried on in large cauldrons, but at the present time evaporating vessels are constructed of well rivetted boiler-plate, the shape being rectangular, the length 10 metres, depth 0·6 metre, and width from 4 to 6 metres. These pans are supported by masonry, which also serves to separate the flues. Over the pans a hood is fixed and connected with a tube carried to the outside of the building to afford egress to the steam. The brine, concentrated to contain from 18 to 26 per cent. of salt, is poured into the pans to a depth of 0·3 metre.

The boiling down process is in many salt works conducted in two different operations:—

a. The evaporation of water to produce a brine saturated at the boiling-point.

b. The boiling down of the saturated brine until the salt crystallises out.

The boiling down is generally carried on for several weeks, the scum being removed, and also the gypsum and sulphate of soda deposited at the bottom of the pan, with perforated ladles. As soon as a crust of salt is formed on the surface of the liquid, a temperature of 50° is maintained. At this stage the salt is gradually deposited at the bottom of the pan in small crystals, and being removed, is put into conical willow baskets, which are hung on a wooden support over the pan to admit of the mother-liquor being returned to it. Finally, the salt is dried and packed in casks.

The quantity of mother-liquor collected after boiling for some two or three weeks is, compared with the quantity of brine evaporated, very small; it was formerly thrown away or used for baths, but is now employed for the preparation of chloride of potassium, the sulphates of soda and magnesia, artificial bitter water, and in some instances for preparing bromine. It is evident that by the boiling down all the salt contained in the brine is not reduced as dry refined salt, a portion being retained among the early deposit formed at the bottom of the pan, another portion remaining in the mother-liquor, and finally some loss accrues from the nature of the operations, amounting generally from 4 to 9·25 per cent. As in some countries salt is an article upon which an excise duty is levied, in order that it may be employed duty free for certain industrial purposes, it is mixed in various proportions with substances rendering it unfit for culinary use.

Properties of Common Salt. Chloride of sodium crystallises in cubes, the size of the crystals determining the varieties known in the trade as coarse, medium, and fine grained salt, and depending upon the rate of evaporation of the brine, a slow evaporation producing very coarse salt. Perfectly pure common salt is not hygroscopic, but the ordinary salt of commerce contains small quantities of the chloride of magnesium and sodium. Usually salt contains from 2·5 to 5·5 per cent. water, not as a constituent, but as an intermixture; hence the phenomenon called decrepitation, due to the breaking up of the crystals by the action of the steam when salt is heated. Ignited to a strong red heat chloride of sodium fuses, forming an oily liquid, and at a strong white heat is volatilised without decomposition. Common salt is readily soluble in water, and is one of the few salts almost equally soluble in cold and in hot water; 100 parts of water at 12° dissolve 35·91 parts of common salt.

In order to express the quantity of salt contained in a brine, it is usual to say the brine is of a particular fineness, strength, or percentage; for instance, a brine at 15 per cent. contains in 100 parts by weight 15 parts of salt and 85 parts of water. The *Grädigkeit* or degree of a brine means the quantity of water which holds in solution 1 part by weight of salt; a brine of 15·6 *Grädigkeit* contains, therefore, 1 part by weight of common salt in 15·6 parts of water. The poundage (*Pfündigkeit*) of a brine indicates in pounds the quantity of salt contained in a cubic foot of brine.

The following table shows the percentage of salt contained in brines of the several specific gravities:—

Salt per cent.	Sp. gr.	Salt per cent.	Sp. gr.	Salt per cent.	Sp. gr.
1	1·0075	7·5	1·0565	16	1·1206
1·5	1·0113	8	1·0603	17	1·1282
2	1·0151	8·5	1·0641	18	1·1357
2·5	1·0188	9	1·0679	19	1·1433
3	1·0226	9·5	1·0716	19·5	1·1510
3·5	1·0264	10	1·0754	20	1·1593
4	1.0302	10·5	1·0792	21	1·1675
4·5	1·0339	11	1·0829	22	1·1758
5	1·0377	11·5	1·0867	23	1·1840
5·5	1·0415	12	1·0905	24	1·1922
6	1·0452	13	1·0980	25	1·2009
6·5	1·0490	14	1·1055	26·39	1·2043
7	1·0526	15	1·1131		

Uses of Common Salt. It is not necessary to enter into particulars on this subject. Salt is used as a necessary condiment to food; a man weighing 75 kilos. contains in his body 0·5 kilo. of common salt, and requires annually 7·75 kilos. to maintain this supply. Common salt is used in agriculture, and is as necessary for cattle and horses as for man. It serves industrially in the preparation of soda, chlorine, sal-ammoniac, in tanning, in many metallurgical processes, the manufacture of aluminium and sodium. Further, it is employed in the glazing of the coarser kinds of pottery and earthenware, from the fact that when common salt is fused with a clay containing iron, the sodium is oxidised at the expense of the iron, and forms soda, which, combining with the alumina and silica, supplies a glaze, while the iron combining with the chlorine is volatilised. The uses of common salt for the preservation of wood, for curing meat, preserving butter, cheese, &c., are too well known to require explanation. Among the salt-producing countries of Europe, England takes the lead, producing annually 32,400,000 cwts., while Germany only produces 10, and Russia 20 million cwts.

MANUFACTURE OF SODA.

(Soda or Sodium carbonate, $Na_2CO_3 = 106$. In 100 parts, 58·5 parts soda and 41·5 parts carbonic acid.)

Soda. All the soda commonly used is derived from the three undermentioned sources:—

α. Natural or native soda;
β. From plants;
γ. Chemical production.

α. *Native Soda.*

Occurrence of Native Soda. Soda is found in many mineral waters, as at Karlsbad, where the waters yield annually 133,700 cwts. of carbonate of soda, and at Burtscheid, Aix-la-Chapelle, Vichy, and the Geyser, in Iceland. Soda occurs as an efflorescence on some kinds of rocks, chiefly of volcanic origin, as trass and gneiss. Sesquicarbonate of soda, $C_3O_8Na_4 + 3H_2O$, is met with in large quantities in the water of the so-called soda lakes of Egypt, Central Africa, the borders of the Caspian Sea and Black Sea, in California, Mexico, and elsewhere. During the hot summer season a portion of the level country of Hungary is covered with an efflorescence of carbonate of soda, locally known as *Székso*, which is collected and brought to market. The Egyptian name for soda is *Tro-Na*, hence the German term *Natron*. The soda locally known in Columbia as *Urao* is obtained from a lake, La Lagunilla, distant 48 miles from the town of Merida. During the hot season the urao crystallises from the water.

and is gathered from the bottom of the lake at a depth of 3 metres by divers, with great risk of their lives; the annual quantity collected amounts to 1600 cwts. When the Spaniards were in possession of this territory the urao was a government monoply, and was brought to Venezuela for the preparation of *Mo* or inspissated tobacco juice. Very recently an inexhaustible supply of native soda has been found in Virginia.[*]

Various theories have been proposed to explain the origin of native soda, but here as in other instances it is best to bear in mind that *a posse ad esse non valet conclusio* Native soda is rarely exported from the countries where it is found and collected, excepting the Egyptian Tro-Na, which is brought to Venetia for glass-making purposes and met with in the trade in the shape of bricks made up with sand.

β. *Soda from Plants, or Soda-ash.*

Soda from Soda Plants, and from Beet-root. When treating in a former chapter of potassa we saw that the ash of plants, especially of those grown at a considerable distance from the sea, contains carbonate of potassa; likewise that plants grown near the sea-shore and in the localities known as salt steppes yield an ash which contains more or less soda in the living plant combined with sulphuric and organic acids, and which under the influence of the carbonate of lime is during the ignition of the plant converted into carbonate of soda. In addition to the species of *Fucus* growing in the sea itself, the genera known as *Salsola*, *Atriplex*, *Salicornia*, &c., are employed for the preparation of soda, and until lately were largely cultivated for this purpose. The process of obtaining soda from these plants simply consists in burning them in pits dug in the sand near the sea-shore, the heat of the combustion becoming so intense as to cause the ash to flux, so that after cooling the material forms a hard slag-like mass, termed in the trade crude soda or soda-ash, the quantity of carbonate of soda it contains varying from 3 to 30 per cent. This new material is refined by exhausting with water and evaporating the liquor. From the different plants and modes of preparation employed we obtain the following distinctions in kind:—

a. Barilla, from Alicante, Malaga, Carthagena, the Canary Islands, and the Barilla soda (*Salsola soda*) produced on the Spanish coast; contains on an average from 25 to 30 per cent. of carbonate of soda.

b. Salicor, or soda from Narbonne, obtained by the ignition of the *Salicornia annua*, planted purposely, and gathered when the seed is ripe; contains about 14 parts of carbonate of soda.

c. Blanquette, or soda from Aigues-Mortes, prepared from the plants growing wild on the tract of comparatively barren land lying between Aigues-Mortes and Frontignan, viz., the *Salicornia Europea, Salsola tragus, Salsola kali, Statice limonium, Atriplex portulacoides.* This soda only contains from 3 to 8 per cent of sodic carbonate.

d. Araxes soda, of about the same value as the preceding, is largely used in Southern Russia, and is obtained from plants of the mountain plateau of the Araxes in Armenia, where the soda is prepared.

e. Of less value even than the preceding is the *Varec soda*, obtained on the coasts of Normandy and Brittany from the *goëmon, Fucus vesiculosus.*

f. Kelp is obtained in Scotland and the Orkneys by the combustion of various sea-weeds, the *Fucus serratus, F. nodosus, Laminaria digitata, and Zostera marina.* Notwithstanding that 480 cwts. of dried plants only yield 20 cwts. of kelp, containing no more than from 50 to 100 lbs. of sodic carbonate, 20,000 people are occupied in the Orkneys alone in the preparation of kelp.

g. Among the varieties of soda derived from plants may be mentioned that obtained in considerable quantity from the vinasse of beet-root, but this soda, according to Tissandier's analysis, always contains carbonate of potassa.

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[*] See "Chemical News," vol. xxi., p. 129.

γ. *Soda prepared by Chemical Processes.*

Soda from Chemical Processes.

M. Leblanc, the inventor of the successful method of converting common salt into carbonate of soda, may indeed be considered as an immediate benefactor to his countrymen, who, until the latter half of the last century, annually paid 20 to 30 millions of francs to Spain for barilla. The war which broke out in 1792 terminated the importation of soda, potash, and saltpetre into France, and hence the Comité du Salut Public decreed in 1793, amongst other measures, that all soda manufacturers should give the fullest particulars of their mode of working, and the processes they imagined might be used on the large scale to obtain soda equally good and cheap as that from barilla without the use of that or any similar material. The manufacturer Leblanc was the first who sent in full particulars on this subject, and his process was declared by the committee to be the best and most suitable, the verdict standing unshaken to the present day, which witnesses the improvement of the recovery of the sulphur from the soda waste.

Leblanc's Process.

This now consists in the following stages:—

a. The preparation of sulphate of soda from salt by the aid either of sulphuric acid or sulphates, or by the roasting of common salt with iron pyrites or other native metallic sulphurets.

b. Conversion of the sulphate into crude soda by roasting with a mixture of chalk and small coal.

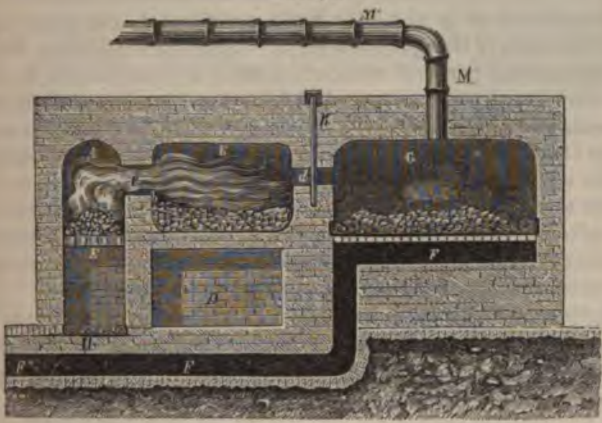
c. Conversion of the crude soda into refined soda or caustic soda by lixiviation and evaporation.

d. Recovery of the sulphur from the soda waste.

Sulphate, or Decomposing Furnace.

a. The most usual mode of converting common salt into sulphate of soda is by the action of sulphuric acid. The condensation of the hydrochloric acid gas is generally effected by a method introduced in 1836 by Mr. Gossage, and consisting in the use of a contrivance known as coke- or condensing-towers. These are square buildings from 12 to 14 metres in height, by an interior width of 1·3 to 1·6 metres, constructed of stone not acted upon by hydrochloric acid, the joints being cemented with a mortar made of coal-tar and fire-clay. To nearly the top these buildings are divided by a wall, each compartment thus formed being filled with pieces of coke resting on a perforated stone floor. Water is caused to flow constantly from the top of the tower on to the coke. The hydrochloric acid gas resulting from the decomposition of the salt by sulphuric acid is conducted by means of stoneware tubes to the bottom of the first compartment of the condensing-tower, and there meeting with the moist coke is condensed to within 95 per cent. of the entire quantity, the other compartment of the condensing-tower being usually in direct connection with the chimney-shaft of the alkali-works. The decomposition-furnaces at first in use were reverberatory furnaces so constructed that the smoke and gases from the combustion of the coals and the hydrochloric acid gas passed off together, and as a consequence the hot gases were not in the best condition for condensation. The furnace now in general use is that invented in 1836 by Gossage, and improved in 1839 by Gamble, who was the first to arrange the two phases or stadia of the decomposition in the separate compartments, G and E, of the furnace exhibited in Fig. 71. This arrangement has been used for a very long period, the alkali manufacturers employing a reverberatory furnace which could be put into communication at pleasure with a kind of muffle, the bottom consisting of a stout cast-iron plate, the flame from the furnace-grate being made to play against this muffle previously to entering the chimney. The muffle communicated with a condensing apparatus, M M′. According to this plan of working, the common salt was placed in G, and well warmed sulphuric acid made to flow over it; a very strong and violent reaction took place, and half or nearly two-thirds of the hydrochloric acid formed was readily condensed, as it was not mixed with the hot gases of the combustion. The product resulting from this mode of operation was a mixture of bisulphate of soda and common salt, $2NaCl + H_2SO_4 = NaHSO_4 + NaCl + HCl$. This mixture was next shovelled into the reverberatory furnace, E, the muffle being again charged with salt and acid. By the intense heat of the reverberatory furnace the mixture of bisulphate of soda and common salt was converted into neutral sulphate, $NaHSO_4 + NaCl = Na_2SO_4 + HCl$; the hydrochloric gas evolved in this operation was, however, condensed with difficulty, in consequence of being mixed with nitrogen, carbonic acid, and carbonic oxide; and besides the condensing towers other and complicated apparatus were required to prevent the escape of acid fumes into the air. These defects have been remedied in the construction of an improved decomposition-furnace.

FIG. 71.



New Decomposition-Furnace. This furnace consists of two muffles, one of cast-iron, the other of fire-bricks; the interior of the former is a segment of a hollow sphere of 9 feet or 2·74 metres diameter, and 1 foot 9 inches or 0·52 metre deep, resting on brick-work. A cast-iron lid is provided, in shape also a segment of a sphere, having a depth in the centre of 1 foot or 0·30 metre; in this lid are arranged two openings with suitable doors, through one of which the common salt is introduced, while the other communicates with the second muffle. The hearth is placed obliquely, the flames first playing on the lid, and then passing under the muffle; accordingly the hydrochloric acid gas is unmixed with other gases, and its temperature being comparatively low, condensation is more readily effected. The second or brickwork muffle encloses a space of 30 feet or 9·14 metres in length, by 9 feet or 2·74 metres in width; under the floor of this room a series of flues or channels are built, while the top is formed of a double vault to admit the circulation of the flames, which are next conducted through the channels under the floor.

The mode of operation is as follows:—Into the iron muffle, previously well heated, half a ton of common salt is introduced, to which is added sulphuric acid of 1·7 sp. gr., the quantity of the acid being regulated so as to leave 1 to 3 per cent. of salt undecomposed in order to obtain a perfectly neutral sulphate. 100 parts of salt require for their complete decomposition 95 parts of an acid at 60° B. = 1·7 sp. gr., or 104 parts of an acid at 55° B. = 1·62 sp. gr. The mixture of acid and salt is occasionally well stirred, and after the lapse of $1\frac{1}{2}$ hour has become sufficiently dry to be raked over into the brickwork compartment of the oven, which is kept at a bright red heat to assist the expulsion of the hydrochloric acid gas. If it is desired to obtain a concentrated hydrochloric acid solution, the escaping gas must be cooled down before entering the condensing-towers. There is generally a valve or damper, by which the communication between the two muffles may be closed, in order that the hydrochloric acid gas evolved in each may be separately collected and condensed. With these contrivances, and well constructed condensers supplied plentifully with water, the preparation of sulphate of soda may be carried on without any inconvenience to the neighbourhood in which the works are situated. For more than twenty years Messrs. Tennant, of Glasgow, have employed this kind of furnace, decomposing 500 tons of common salt per week without receiving any complaints. On the Continent, alkali-works are legally compelled to have the decomposition-furnaces constructed according to a plan first brought out in Belgium, and which is very similar to the furnace already described. The assertion of Dr. Wagner, in his original text, concerning the many complaints now arising in England in reference to the escape of hydrochloric acid fumes from alkali-works, is altogether unfounded, the fact being that according to the published reports of the inspector, Dr. Angus Smith, under the Alkali Act, nearly all the manufacturers condense, instead of 95 per cent. of the hydrochloric acid, as required by the Act, from 97 to 98·5 per cent.

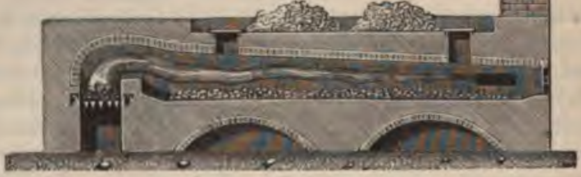
Conversion of the Sulphate into Crude Soda.

b. In order to convert the sulphate of soda into crude or raw sodic carbonate, the former salt is mixed with chalk, or sometimes with slaked lime and small coal, and this mixture, fused in a reverberatory furnace. According to Leblanc's directions, the proportions are—

Sulphate	100 parts
Chalk..	100 ,,
Slaked lime	50 ,,

but the quantities as employed in ten different works vary for 100 parts of sulphate from 90 to 121 parts of chalk, and the quantity of small coal from 40 to 75 parts.

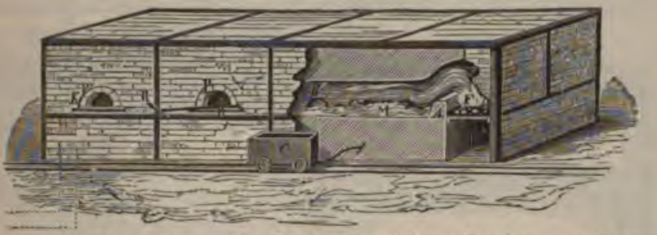
FIG. 72.



In some alkali-works for a portion of the chalk is substituted the desulphurised and lixiviated soda waste. The reverberatory furnace generally used in English alkali-works, and technically known as a *balling furnace*, is shown in Fig. 72, and that employed in Germany in Fig. 73. In England, the materials having been first heated on the upper stage of the furnace by the waste heat, only remain in the *working furnace* (see Fig. 72) for about half-an-hour; in German works the mixture of sulphate, chalk, and small coal is strongly heated in M (see Fig. 73), until the mass becomes fluxed and pasty, and lambent flames of burning carbonic oxide are ejected from the surface. When this is seen the semi-fluid mass is removed from the furnace through the openings P P, and transferred to an iron car, C, where it is left to cool.

It is difficult to say whether the English or Continental method is the more preferable; viewed from a theoretical point of view, it would appear that the English method is the better of the two. As in English works, a smaller quantity of materials, only about 7 cwts., while in Continental works from 30 to 70 cwts., is operated upon at a time, the labour is lighter; the materials, too, are not exposed to an intense heat for a long period; thus a loss of soda by the volatilisation of the sodium is less likely to occur. According to Wright's investigations (1867), the loss of soda by the conversion of the sulphate amounts to 20 per cent. of the sodium contained in the sulphate, as shown by the following figures:—

FIG. 73.

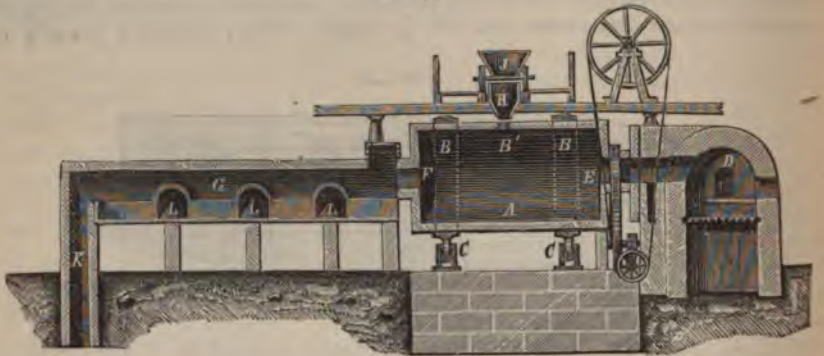


Undecomposed sulphate	3·49
Insoluble sodium compounds	5·44
Volatilisation of the sodium	1·14
Sodium retained in the waste	3·61
Loss occasioned by the evaporation of the liquors	6·56
	20·24

Soda Furnace with Rotatory Hearth.

In 1853 Elliot and Russell suggested a contrivance which dispensed with the stirring of the materials by manual labour, and consisted of a cylindrical vessel made to rotate on a horizontal axis. Stevenson and Williamson improved upon this idea, and according to their plan of working (see Fig. 74) the mixture of sulphate, chalk, and small coal is placed in the iron cylinder, A, lined with fire-clay. Ribs or rails, B, cast on the cylinder, run on the wheels, C, receiving motion from machinery with which they gear, and causing the cylinder to rotate. The heated air of the hearth, D, flows through the opening E into the cylinder, and passing through F, reaches the vaulted compartment, G, and is carried off by the flue, K, to the chimney. The interior of the cylinder having been heated to redness, the materials are allowed to fall into it from the waggon, J, through the funnel, H. After the lapse of ten minutes the cylinder is caused to make a half revolution, and is then left for five minutes, the operation being continued until the mass inside the cylinder fuses, which takes place in about half-an-hour. The cylinder is then set continuously in motion so as to make one revolution every three minutes. The progress from time to time is watched through a door-way constructed in the cylinder, and as soon as the operation is complete the molten mass is run off through the opening B′. There can be no doubt that the rotatory furnace is a great improvement, and one which, besides saving labour, prevents a loss of soda by volatilisation. A cylinder 11 feet long and 7·5 feet in diameter converts in two hours 14 cwts. or 700 kilos. of sulphate at an expenditure of only 2s. 1d.

FIG. 74.



The composition of the crude or *ball* soda is approximately :—

Carbonate of Soda	45
Sulphuret of calcium ..	30
Caustic lime	10
Carbonate of lime	5
Foreign substances	10
	100

In this country large quantities of soda ash are used in glass-making, soap-boiling, bleaching, and other operations.

Lixiviation of the Crude Soda.

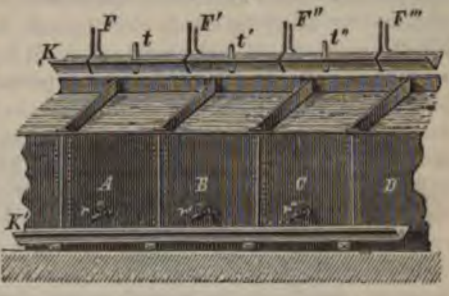
c. Conversion of crude into refined soda by lixiviation and evaporation. *a.* Lixiviation of the crude soda. When the crude soda is acted upon by water there results a solution containing chiefly carbonate of soda, and a mass remaining undissolved known as soda waste. 100 parts of raw soda yield :—

Soluble matter	45·0 parts
Soda waste	58·7 ,,
	103·7 ,,

As a rule English ball soda has a deeper colour, and contains more carbon than the soda of Continental manufacture. Ball soda, previously to being lixiviated, is usually exposed for at least two and sometimes for ten days to the action of the air, to gain in porosity, and hence be more readily acted upon by the water.

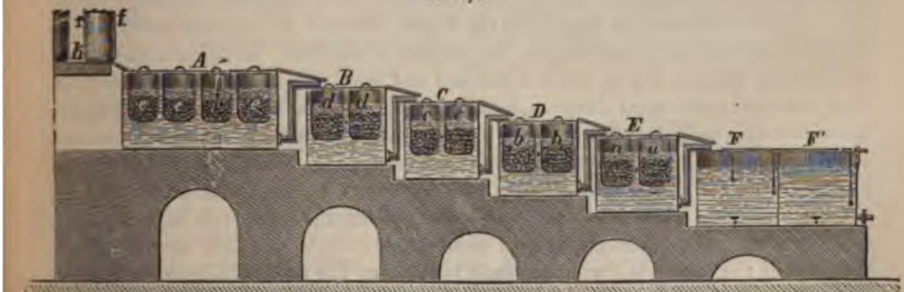
Of the several methods of lixiviation proposed, and in more or less successful use on the large scale, may be mentioned the following :—The method of lixiviation by simple filtration is not to be recommended on account of the great labour it requires, but the process consists in putting the crude soda, previously broken up into lumps of suitable size, into tanks provided with a perforated false bottom, upon which the crude soda is placed, water being poured on. This arrangement is represented in Fig. 75, A, B, C, D. The perforated false bottom is about 25 centims. from the bottom of the tanks. The wooden channel, K, suspended from the ceiling of the shed by the iron bands, F F', conveys water, which by means of the plugs, t, t', and t'', can be let into the tanks, these being provided with taps, r, r', and r'', by which the liquid can be run off into the channel, K'. To illustrate the *modus operandi* three tanks, A, B, C, are sufficient; A is filled with fresh ball soda, B with ball soda once, and C with ball soda twice lixiviated. We then begin by filling each tank with the liquor which has been used for washing the soda waste the last time before throwing it aside; this liquid remains in each tank for a period of eight hours, and the alkaline ley, which then marks 30° B., is run off from A, and the operation repeated with weaker liquors in B and C, the leys being all conveyed to a large reservoir, the contents of which mark 25° B. Fresh liquor is poured into A and B, and into D, which is filled with ball soda. By this arrangement a constant supply of ley at 25° B. is kept up.

FIG 75.



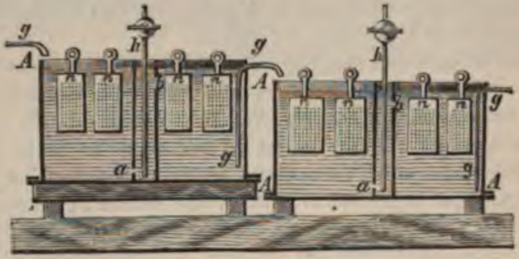
Desormes's lixiviation apparatus, Fig. 76, consists of a series of twelve to fourteen tanks, of which only five, A, B, C, D, E, are exhibited in the woodcut. By means of the bent tubes, fitted about 15 centims. from the bottom of each tank, the liquor flows into the next lower tank of the series, and so to the tanks, F F', called the clearing or settling tanks, of which there are six connected together by tubes. The ball soda to be lixiviated is ground to powder, and placed in the perforated sheet-iron vessels, *e e*, *a d*, and so on. At the commencement the tanks are filled with

FIG. 76.



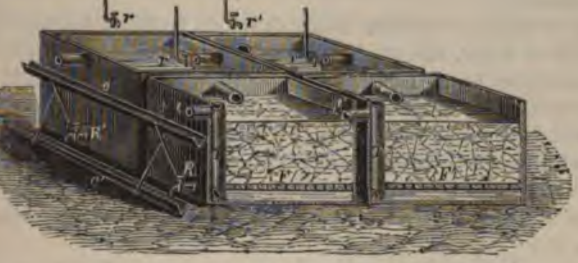
warm water, and two perforated vessels placed in E filled with 50 kilos. of ball soda; after twenty-five minutes these vessels are removed to D, and others filled with fresh soda placed in E. In this manner the operation proceeds, so that after eight hours, when fourteen lixiviation tanks are worked, there are found in A perforated vessels which have been gradually removed from the lowest to the highest tank, A, two vessels, *f f*, having been removed from that tank and placed upon the shelf, *k*, to drain, where having remained for about half-an-hour they are removed, the contents emptied, and other vessels placed to drain. Each time that two of the perforated vessels filled with ball soda are placed in the lowest tank, there is poured into the uppermost as much water as corresponds with the bulk of the fresh soda; this water displaces the heavy ley which runs through the tube from A to B, and so on, until at last the concentrated and nearly saturated liquor runs from E into F F, where any suspended matter is deposited. The temperature of the liquor in these tanks should be from 45° to 50°; but not higher, in order to prevent any decomposition of the sulphide of calcium. The lixiviation tanks, as well as the clearing tanks, are provided with steam pipes for the purpose of keeping the liquor sufficiently heated, and to prevent any soda crystallising out by cooling. It is almost evident that this method of lixiviation is the best which can be adopted, as the concentrated liquor cannot adhere to the solid substance which it is intended to dissolve, because in consequence of its high sp. gr. the liquor sinks to the bottom of the tank. Fig. 77 represents two lixiviation tanks drawn to a larger scale, and of a somewhat different arrangement. Each tank is divided into three compartments by means of a double partition wall, communication between the two compartments being provided by the ncles *a* and *b* and the space between the partition plates receiving the steam pipes, *h h*. *g g* are the tubes for conveying the liquor, and *n n* the perforated vessels, to which are rivetted iron bars serving the purpose of handles. Mr. James Shanks, of St. Helen's, was the first to found a rational and economical plan of lixiviation, on what is termed methodical filtration, based upon the fact that a solution becomes more dense the more saline matter it has in solution, and that a column of weak ley of a certain height equilibrates a shorter column of a stronger ley. In accordance with this principle, the tanks, four or eight in number, are placed as shown in Fig. 78, and through them water is caused to flow, exhausting the crude soda in its passage, and becoming consequently denser in each consecutive tank of the series; hence, the level of the liquid is lowered in each tank from the first, which contains pure water, to the last, from which a saturated ley runs off. The length of the tanks is 2·6 metres by 2 metres in depth; F is a perforated false sheet-iron bottom supported by iron bars. From the bottom of each tank an open tube, T, the lower opening being cut diagonally, and at the top a smaller tube, *t*, soldered on, connect the tanks. The water pipes, *r r r r*, fitted with taps are placed to admit of water being supplied to each tank; by means of the taps, R R′, the ley can be run off into the channel, *c*′. Four lixiviations as a rule suffice. The working is as follows:—The

FIG. 77.



first tank contains ball soda already three times lixiviated; the liquor added to it is a very weak soda solution from a former operation, which percolates into the second tank. The liquid there meets with soda which has been twice submitted to the lixiviation process, and next flows over into the third tank, the solid contents of which have been only once previously lixiviated. Finally, the lye arrives in the fourth tank, in which fresh ball soda has been placed, and from this tank flows into a large reservoir. The first tank having been cleared of soda waste is now filled with fresh ball soda, and the succession of the operation reversed by the aid of taps fitted to the tubes connecting the tanks. The larger the number of tanks the more rapidly within certain limits a given weight of crude soda can be exhausted. The density of the ley ought to be from 1·27 to 1·286, a cubic foot, or 0·028 cubic metre, containing from 4·5 to 4·95 kilos. of solid matter. The advantages of this mode of lixiviation are—1. That the carriage of the crude soda from one tank to another is dispensed with, and consequently much labour saved. 2. The soda being always covered with liquid cannot cake. 3. As the current is always downwards the most concentrated portion of the fluid is conveyed forward, and consequently less water is required. 4. By the continuity of the operation any reaction between the alkali and the insoluble calcium sulphuret is prevented, or, in other words, the formation of soluble alkaline and other sulphurets, entailing a loss of soda, is reduced to a minimum. 5. The high degree of concentration of the ley effects a considerable saving in the expense of the evaporation.

FIG. 78.



The nature of the ley after the suspended matter has been deposited, greatly depends upon the condition of the ball soda employed, the duration of the process, and the temperature of the water; it is, therefore, difficult to make any general observation. Kynaston, Scheurer-Kestner, and Kolb have proved that ball soda does not contain caustic soda, and that consequently the presence of this substance in the ley is due to the action under water of the lime upon the sodic carbonate. Sulphuret of calcium can only be present in the dry ball soda in very small quantities, but sulphuret of sodium may exist in the ley to a greater extent than caustic soda, the quantity varying with the mode of lixiviation. Commonly, only monosulphuret of sodium is present in the ley; even if a polysulphuret were temporarily formed it would be immediately converted into monosulphuret by the presence of the caustic soda. The dry ball soda contains peroxide of iron, converted into sulphuret of iron by the action of the water; this sulphuret dissolving in the sulphuret of sodium causes the green- or yellow-brown colour of the ley. The quantity of water employed in the lixiviation has no effect upon the causticity of the ley, but the quantity of sulphuret of sodium increases with the quantity of water, the duration of the lixiviation, the temperature, and the concentration; this is owing to the increased solubility of the sulphuret of calcium, which, when in contact with water, is converted into hydrosulphuret of calcium and hydrate of lime, the former yielding with caustic soda the more sulphuret of sodium the higher the concentration of the ley. The same reasoning holds good for carbonate of soda, which is also converted into sulphuret, but only in very dilute solutions, at a higher temperature after a lengthened contact.

According to Kolb's researches, ball soda should be lixiviated rapidly, with but a small quantity of water, and at a low temperature. If it were possible it would be a great improvement to contrive an apparatus in which ball soda could be lixiviated in a few hours with only so much cold water as would yield a very concentrated ley; the liquors obtained under such conditions would be free from sulphuret of sodium.

The following analysis will give some idea of the composition of the crude ley. The sample was obtained from the alkali-works of Matthes and Weber, at Duisburg, the sp. gr. = 1·25, 1 litre containing 313·9 grms. of solid saline matter, consisting in 100 parts of—

Carbonate of soda	71·250
Caustic soda	24·500
Common salt	1·850
Sulphite of soda	0·102
Hyposulphite of soda	0·369
Sulphuret of sodium	0·235
Cyanide of sodium	0·087
Argillaceous earthy matter	1·510
Silica	0·186
Iron	traces
	100·089

Another crude ley from some works near Aix-la-Chapelle was of a sp. gr. = 1·252, and contained 311 grms. of solid matter per litre.

Evaporation of the Ley.

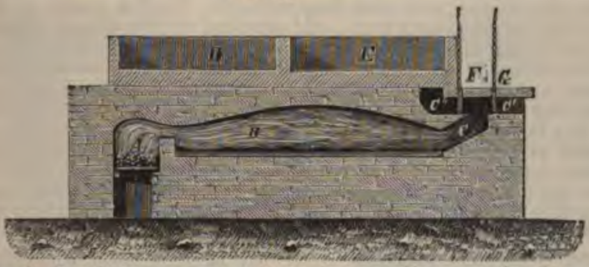
β. The clarified liquor contains essentially carbonate of soda and caustic soda, with common salt and other soda salts in smaller quantities. Owing to the presence of the double sulphuret of iron and sodium, the ley is coloured during the evaporation, if it be performed with the liquor immediately from the lixiviation tanks; to prevent this result it is necessary that the leys should stand for a considerable time in the clearing reservoirs to effect a slow oxidation of the compound salt, more rapidly attained by forcing a current of air through the ley, as suggested by Gossage. Bleaching-powder and nitrate of soda are used as oxidising agents; a lead-salt, oxide of copper, and spathose iron ore have been employed. As Kolb's researches have proved that monosulphuret of iron is insoluble in caustic and in carbonate of soda solutions, an addition of sulphate of iron will have the effect of converting the double sulphuret of iron and sodium into monosulphuret of iron and sulphate of soda, the former salt settling rapidly and yielding a clear colourless liquid, and on evaporation a colourless salt.

The ley is treated in either of the two following ways:—

a. Evaporated to dryness, the result being a homogeneous product which contains unaltered all the constituents of the ley, including the caustic soda.

β. The ley is evaporated to a certain degree of concentration, the supersaturated solution depositing on cooling carbonate of soda as a crystalline powder, containing 1 molecule of water, $Na_2CO_3 + H_2O$; the salt is gradually removed from the liquor by perforated ladles. During the evaporation fresh ley is run into the pan from a reservoir at a higher level, and in this way the operation is continued for several months. It is clear that by conducting the evaporation in this manner, the carbonate of soda collected becomes gradually less and less pure, being mixed with chloride of sodium and sulphate of soda; at last a mother-ley is left, containing chiefly caustic soda and sulphuret of sodium, and in a concentrated solution of these substances the other salts are insoluble. The crystalline carbonate of soda is first drained, an operation sometimes performed in centrifugal turbines, and then calcined in a reverberatory furnace to oxidise any sulphuret of sodium that might be present; after this calcination the salt constitutes the calcined soda of commerce. The quality of the commercial article varies considerably, the difference being partly due to the care taken in the evaporation. The first crop of salt is always the best, that is to say, contains the largest percentage of sodic carbonate, sometimes amounting to 90 per cent. When the ley is to be evaporated to dryness, the operation is carried on in a reverberatory furnace, Fig. 79. The hearth is floored with fire-bricks, on to which a thick coating of carbonate of soda is well rammed. The fuel burning in A is coke; as soon as the furnace has become thoroughly red-hot, ley previously evaporated to 33° B. in the pans D and E, is run into the furnace, effecting a very rapid evaporation to dryness, care being taken to stir the saline mass to keep the salt in a pulverulent state. By means of the dampers, F, G, and the flues, C C′, the hot air and flame of the burning fuel may be conducted under the pans D and E or into the chimney. The composition of soda thus evaporated to dryness is, according to the analysis of two samples by Mr. J. Brown, as follows:—

FIG. 79.



	I.	II.
Carbonate of soda	68·907	65·513
Caustic soda	14·433	16·072
Sulphite of soda	7·018	7·812
Hyposulphite of soda	2·231	2·134
Sulphuret of sodium	1·314	1·542
Chloride of sodium	3·972	3·862
Aluminate of soda	1·016	1·232
Silicate of soda	1·030	0·800
Insoluble matter	0·814	0·974
	100·735	99·941

The salt is next calcined, and the sulphuret of sodium converted into sulphite of soda, a portion of the caustic soda being converted into carbonate of soda. The calcined salt is now ready for the market; but in some of the large alkali-works near Newcastle-on-Tyne it is re-dissolved in water, treated with carbonic acid, and again evaporated. A better product results from another method, namely, evaporating the ley to a known degree of concentration, and obtaining small crystals of soda-salt ($Na_2CO_3 + H_2O$). In this case, as regards the methods of evaporation employed, the two following are most general:—Heat is brought to bear on the surface of the liquid contained in shallow rectangular iron pans fitted to the hearth of a reverberatory furnace; the liquid rapidly boils at the surface, and a saline crust is formed, which is constantly broken up and collected with iron rakes by the workmen. Now and then the salt deposited at the bottom is removed and placed on a sloping ledge to drain. This method of evaporation is economical, but attended with the disadvantage that the ley is constantly in contact with the carbonic and sulphurous acid gases arising from the combustion of the fuel, the consequence being that a portion of the caustic soda is converted into carbonate and sulphite of soda, the latter by the subsequent calcining operation being converted into sulphate. By the second plan of evaporation the heat is conveyed to the bottom of the pans, but then many precautions are required to prevent the bottom being burned in consequence of the settling down of a saline mass not conducting heat. Mr. Gamble, at St. Helens, employs a pan of a peculiar form, the section being like that of a boot; it is heated by the waste heat of the soda furnace, and the inclination of the sides of the pan greatly assists the removal of the salt, which, having been drained, is calcined, yielding a grey-coloured salt, afterwards purified by solution with the aid of steam in a small quantity of water, decanting the clear solution, and again evaporating it. Ralston obtains a purer product by washing the impure carbonate with a cold saturated solution of pure carbonate of soda, the chloride and sulphuret of sodium and the sulphate being thus removed. As already stated, the evaporation is not always continued to dryness, but to a degree of concentration determined by experience. By varying the relative bulk of the liquid a more or less pure product may be obtained; when, for instance, the ley of the lixiviation tanks (= 1·286 sp. gr.) is evaporated to $\frac{7}{12}$ths of its bulk, and the salt separated removed, this salt corresponds to a purified soda salt of 57 per cent.; by evaporating the remaining liquid to $\frac{3}{4}$ths of its bulk, a salt of 50 per cent. is obtained. When the mother-liquor is evaporated to dryness, a very caustic and impure salt is obtained. Kuhlmann, at Lille, employs pans which are graduated so that the bulk of the liquid may be readily ascertained for the purpose of fractioned evaporation. The purification of the crude ley, containing sulphuret of iron dissolved by sulphuret of sodium, may be effected, as suggested by Gossage, in 1853, by filtering the liquid through a coke-tower (one of the towers used for condensing hydrochloric acid), a current of air being forced upwards to assist in oxidising the sulphuret of sodium.

The composition of refined soda, according to Tissandier's analyses, is:—

	1.	2.	3.	4.	5.
Moisture	2·22	3·11	1·15	1·00	0·40
Insoluble matter..	0·12	0·22	0·08	—	0·06
Chloride of sodium	12·48	6·41	3·28	2·11	0·99
Sulphate of soda	8·51	3·25	2·15	1·50	0·35
Carbonate of soda	76·67	87·01	92·34	95·39	98·20
	100·00	100·00	100·00	100·00	100·00

The composition of soda, containing caustic soda, is:—

	1.	2.	3.	4.
Moisture	2·10	1·50	2·48	1·38
Insoluble matter	0·12	0·11	0·21	0·09
Chloride of sodium	4·32	2·43	3·50	4·11
Sulphate of soda	8·80	1·62	2·15	2·50
Carbonate of soda	82·47	88·09	84·54	81·67
Caustic soda	2·11	6·25	7·12	10·25
	100·00	100·00	100·00	100·00

In order to obtain crystallised soda, $Na_2CO_3 + 10H_2O$, with 63 per cent. of water, a saturated solution of calcined soda in hot water is poured into large iron vessels, and yields crystals on cooling. The calcined soda is generally dissolved in conical vessels (Fig. 80), made of boiler-plate. C is a steam-pipe, B a water-pipe, D a perforated vessel to contain the calcined soda to be dissolved. The boiler is three-fourths filled with water, the perforated vessel filled with soda is then lowered into the liquid, and the steam turned on. The soda is rapidly dissolved, and when the solution marks 30° to 32° B. it is run into the crystallising vessels; the crystallisation is complete in five to six days in moderately cool weather. The crystals are broken up, and again dissolved in water in the vessel A (Fig. 81), heated by the fire at C. D D are flues carrying flame and heated air round the vessel; B is a water-pipe. The vessel having been filled with crystals, a small quantity of water is added, and as soon as the salt is completely dissolved, the fire is extinguished, the liquid being left to settle. The clear liquid is next syphoned into a reservoir, and from this poured into cast-iron crystallising vessels. After seven or eight days the mother-liquor is removed, and the crystals are detached from the surface of the iron by placing the crystallising vessels for a few moments in hot water, the result being that by the incipient fusion of the crystals in their water of crystallisation, they are loosened from the metal to which they adhere. After, draining the salt is dried in rooms heated to 15° to 18°, and then packed in casks. Although a crystalline salt is generally purer than a non-crystallised mass, yet the large quantity of water contained in crystallised carbonate of soda is an impediment to its extensive use, both on account of expense of carriage and the weakness of the alkali. In this country, however, owing to the great facility of water carriage, crystallised carbonate of soda is very largely used.

Fig. 80.

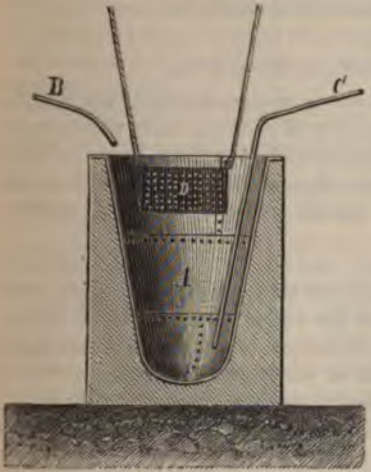
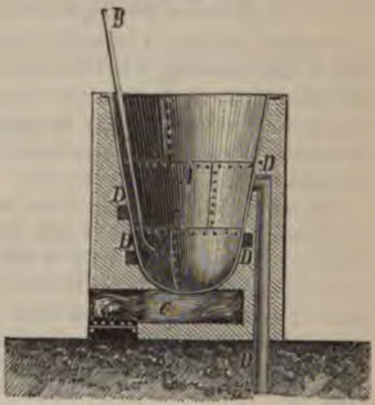


Fig. 81.



Theory of Leblanc's Process. The process of M. Leblanc has been best elucidated by the more recent researches of Gossage and Scheurer-Kestner. Formerly it was assumed that when a mixture of sulphate of soda, carbonate of lime, and carbon were calcined, the carbon while yielding carbonic oxide converted the sulphate of soda into sulphuret of sodium, in its turn decomposed by the carbonate of lime, the result being the formation of carbonate of soda, oxysulphuret of calcium, and the evolution of a portion of the carbonic acid; (*a*) $Na_2SO_4 + 2C = Na_2S + 2CO_2$;

(β) $2Na_2S + 3CaCO_3 = 2Na_2CO_3 + CaO,2CaS + CO_2$. According to Unger the carbonate of lime loses its carbonic acid as soon as sulphuret of sodium is formed, there remaining a mixture of caustic lime, sulphuret of sodium, and carbon, which becomes converted into oxysulphuret of calcium, and caustic soda, the latter by taking up the carbonic oxide resulting from the combustion of the carbon becoming sodium-carbonate; this view appears to be nearest the truth, but as proved by Scheurer-Kestner, Dubrunfaut, J. Kolb, and Th. Petersen, it is not necessary to assume the existence of oxysulphuret of calcium for the purpose of explaining the fact that the sulphuret of calcium does not act upon the sodium-carbonate, because sulphuret of calcium is almost insoluble in water, 12·5 parts of water dissolving at 12·6° only 1 part of sulphuret of calcium. This view is also confirmed by the results of experiments made by Pelouze. During the formation of soda in the calcining furnace the carbon is only converted into carbonic acid, viz.:—

α. $5Na_2SO_4 + 10C = 5Na_2S + 10CO_2$.

β. $5Na_2S + 7CaCO_3 = 5Na_2CO_3 + 5CaS + 2CaO + 2CO_2$.

However, as there is formed during the calcination process, especially towards the end of this operation, a not inconsiderable quantity of carbonic oxide which burns off with a bluish flame, this substance, although a secondary product, has to be taken into account in the formula; moreover, the formation of this gas is important, for as soon as it makes it appearance the chief reaction is being completed, proving the heat to be at its proper degree.

The researches of Unger have undoubtedly proved that when the sulphate is reduced by carbon there is only carbonic acid and not a trace of carbonic oxide formed, so that carbonic oxide is the result of the action of the excess of carbon upon the carbonate of lime; this reduction of the carbonate of lime by carbon takes place at a much higher temperature than that at which the sulphate is reduced, therefore the formation of carbonic oxide takes place after that of the carbonate of soda. Consequently there must be distinguished three phases in the formation of soda, viz.:—

α. The reduction of the sulphate, with evolution of carbonic acid gas—

$$(Na_2SO_4 + 2C = Na_2S + 2CO_2).$$

β. Double decomposition of the newly formed sulphuret of sodium and carbonate of lime ($Na_2S + CaCO_3 = Na_2CO_3 + CaS$).

γ. The reduction of the excess of carbonate of lime by the carbon—

$$(2CaCO_3 + 2C = 2CaO + 4CO).$$

During the lixiviation the presence of caustic lime aids the formation of caustic soda. According to theory, 100 parts of sulphate only require 20 of carbon, but it is the practice to employ an excess of carbon, as much as 40 to 75 per cent., to provide against incomplete mixture, the combustion of carbon without effect, and because of the necessity of obtaining the reaction of the carbonic oxide in order that the progress of the operation may be observed, as experience has proved that the mass should not be removed from the furnace until this combustion is nearly over.

Utilisation of Soda Waste. The greater part of the soda now employed is obtained by Leblanc's process, which, while it admits of lixiviating the soda readily and completely, is defective, inasmuch as the residue, or waste as it is technically called, contains nearly all the sulphur used in the manufacture; and that this is not a slight loss may be inferred from Oppenheim's statement, that in the alkali works at Dieuze, Lorraine, the accumulated waste contains an amount of sulphur valued at £150,000. For every ton of alkali made there is accumulated 1½ tons of waste, containing 80 per cent. of the sulphur used in the manufacture; and this waste, until lately thrown on a refuse heap in some fields adjacent to the works, often proved a nuisance in hot weather, giving rise to fumes of sulphuretted hydrogen. For the last forty years much time and money have been spent in trying to recover the sulphur, but not until 1863 was any attempt successful. Three different processes are now resorted to, viz.—Guckelberger's, modified and practised by Mond; Schaffner's plan; and the process invented by M. P. W. Hofmann, at Dieuze. Since the first successful experiment the methods have been so rapidly improved that, at the Paris Exhibition of 1867, no fewer than nine samples of recovered sulphur were sent in. All the methods mentioned above are based upon the same principle—the conversion of the insoluble sulphurets of calcium contained in the waste into soluble compounds by the aid of the oxygen of the atmosphere; the lixiviation of the oxidised mass, and precipitation of the sulphur contained in the leys by a strong acid, practically hydrochloric acid.

Schaffner's Sulphur Regeneration Process.

M. Schaffner's plan for the regeneration of sulphur from soda waste involves the following operations:—

α. Preparation of the liquor containing sulphur
β. Decomposition of the liquor.
γ. Preparation of the sulphur.

α. The soda waste is submitted to a process of oxidation by the action of the air, and for this purpose is placed in large heaps, where heating takes place, together with the formation of polysulphurets and subsequently hyposulphites. After a few weeks the interior of the heap assumes a yellow-green colour, when the material is ripe for lixiviation; the heap is then broken up into large lumps, which remain for another twenty-four hours' oxidation. These lumps are next submitted to lixiviation with cold water, and a concentrated liquor obtained. After this process follows another oxidation, effected by placing the lixiviated residues in a pit dug in the soil to a depth of 1 metre, and situated close to the lixiviation tanks; by this burying the heat generated by the oxidation suffers less dissipation than when the material is exposed on all sides to currents of air. The second oxidation proceeds more rapidly than the first in consequence of the greater porosity of the mass, so that besides polysulphurets more hyposulphites are formed. Instead of effecting the second oxidation by burying, the waste may be left in the lixiviation tanks, and the oxidation accelerated by forcing the hot gases from a chimney under the perforated bottom of the tank; by these means both time and labour may be saved, the oxidation being complete in 8 to 10 hours. According to the quality of the alkali waste, this process of oxidation may be repeated three to four times; the gases accompanying the smoke of burning fuel are exceedingly well suited for effecting the decomposition of the sulphuret of calcium in such a manner as to cause the formation of polysulphurets and hyposulphites. The liquors resulting from the first lixiviation contain chiefly polysulphurets and hyposulphites; but the liquors obtained after the second and third oxidation contain essentially hyposulphites; all the liquors are collected in one reservoir.

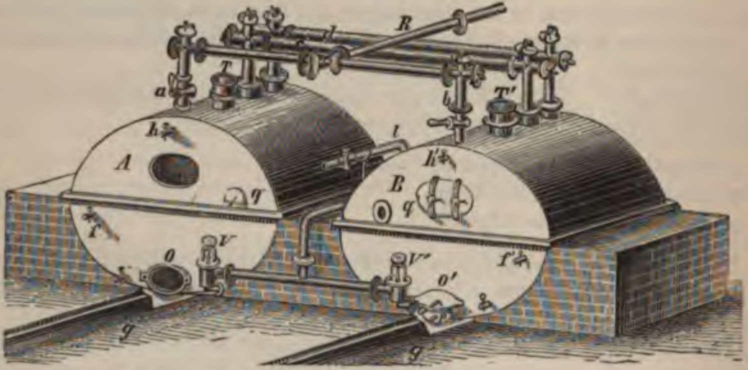
β. The decomposition of the lixiviation liquor by means of hydrochloric acid is carried on in a closed apparatus of cast-iron or stone, and is based upon the fact that, hyposulphites when treated with hydrochloric acid, evolve sulphurous acid gas, sulphur being precipitated ($Ca_2O_3 + 2HCl$ yields $CaCl_2 + SO_2 + S + H_2O$), and upon the reaction exerted by sulphurous acid upon the polysulphuret, which, while sulphur is deposited, is again converted into hyposulphite of lime—

$$(2CaSx + 3SO_2 = 2CaS_2O_3 + Sx).$$

The liquor is tested by titration to determine the quantity of polysulphuret and of hyposulphites contained, and according to the result the residue is more or less oxidised.

The apparatus generally employed in the decomposition is shown in Fig. 82; A and B are the vessels to contain the liquor; *l* is the pipe by which the liquor is conveyed to A or B, regulated by a piece of elastic tubing entering at *q* into A, or *q′* into B. T and T′ are earthenware tubes by which the hydrochloric acid is introduced. *e* and *d* are glass tubes, *e* is fitted to the top of A, and has a longer leg dipping into the fluid at B; the reverse is the case for *d*, the short leg of which is fitted to B, while the longer leg dips into the fluid in A. The tap, *a*, is closed when the gases should enter through *e* into the fluid contained in B, but the tap, *b*, is shut, and *a* opened, when the gases passing through *d* are to enter the fluid contained in A. The excess of gas is carried off by the tube R. As soon as the decomposition by the action of the hydrochloric acid is effected, steam is injected through the valves, V V′, to expel the last traces of sulphurous acid from the liquor. The liquor and finely divided sulphur are run off at O and O′, care being taken to let the chloride of calcium solution run off by removing the wooden plug, *p*. In order to ascertain whether all the sulphurous acid is expelled, the wooden taps, *h h′*, are opened, the smell of the gas being a sufficient indication of its presence. The taps, *f* and *f′*, are employed as test cocks to ascertain the progress of the operation, and also to see whether the vessels are properly filled with liquor.

FIG. 82.



The sulphur obtained by this process is fine-grained, and mixed with some gypsum, chiefly due to the sulphuric acid contained in the hydrochloric acid. The sulphur and chloride of calcium liquor are conducted by the spout, *g*, to a vessel with a false bottom, perforated and covered with a flannel cloth, through which the liquor passes, the sulphur being retained.

γ. The sulphur is prepared for the market by a very simple process. It is mixed with sufficient water to constitute a paste, which is put into a cast-iron vessel, and steam at a pressure of $1\frac{2}{3}$ atmospheres admitted to melt the sulphur, the water taking up any adhering chloride of calcium solution, and also the gypsum. The molten sulphur collects in the bottom of the vessel, and is tapped off into moulds; the supernatant liquor does not mix with the sulphur owing to the greater specific weight of the latter. In order to perfectly saturate any free acid which might still be present some milk of lime is added; by this addition another end is gained, viz., the removal of any arsenic, in the following manner:—If during the melting process an excess of lime be present, sulphuret of calcium is formed, and this sulphuret dissolves any sulphuret of arsenic which is thus removed to the supernatant liquor. The advantages of melting and purifying the sulphur by the above process are—the sulphur need not first be carefully washed and dried, fuel is saved, the sulphur freed from arsenic, and brought to the best state for pouring into moulds. Figs. 83 and 84 represent the melting vessel; the cast-iron cylinder, B, is surrounded by a wrought-iron cylinder, A, and the whole inclined to admit of the molten sulphur collecting at the lower part of B. The sulphur paste is being stirred by an apparatus in gearing at R with some motive power. The paste is poured into B at *m*; at *a* steam is introduced, passing at *o* into the inner cylinder, and let off, when the melting is finished, through *d* and the valve, *v*; the molten sulphur is run off at *z*; S is a safety valve. By this process 50 to 60 per cent. of the sulphur contained in the soda waste is recovered, for every cwt. recovered 2 to 2¼ cwts. of hydrochloric acid being employed. If this acid were too expensive, the residues of chlorine manufacture might be used, these residues consisting mainly of chloride of manganese, free hydrochloric acid, and chloride of iron; the first step would then be to free these residues from the chloride of iron by means of the lixiviated soda waste added in small quantities at a time; sulphuretted hydrogen would be given off, and Fe_2Cl_6 reduced to $FeCl_2$, the changed colour indicating the end of the reaction. The dirty grey-coloured sulphur from this reaction should be burnt in the pyrites or sulphur-burning furnace. The prepared residue would now be fit for employment as a substitute for hydrochloric acid. Should, however, some monosulphuret of calcium be present in the soda waste liquor—not a very likely occurrence—some hydrochloric acid must be added before using the residues.

FIG. 83.

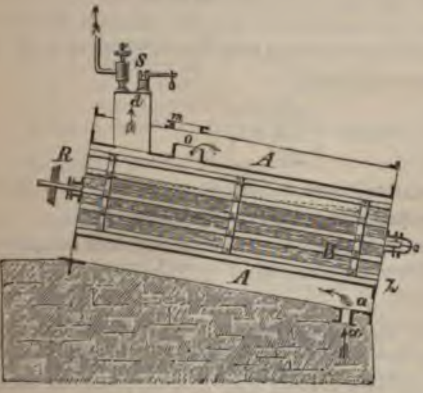
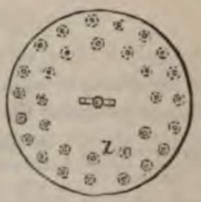


FIG. 84.



Sundry Methods of Preparing Soda from Sulphate of Soda.

Among the many methods which have been proposed for the preparation of soda the following especially deserve notice. According to Kopp's methods of soda manufacture sulphate of soda, oxide of iron, and carbon are smelted together in an ordinary soda furnace:—

$$\left.\begin{array}{l}2Fe_2O_3\\3Na_2SO_4\\16C\end{array}\right\}\begin{array}{c}\text{yield by}\\\text{calcination}\end{array}\left\{\begin{array}{l}Fe_4Na_6S_3.\\14CO.\\2CO_2.\end{array}\right.$$

The crude soda absorbs from the air water, oxygen, and carbonic acid, becoming converted into carbonate of soda and an insoluble residue of sulphuret of iron containing sodium, $Fe_4Na_6S_3$:—

$$\left.\begin{array}{l}Fe_4Na_6S_3\\2O\\2CO_2\end{array}\right\}\text{ yield }\left\{\begin{array}{l}2Na_2Co_3.\\Fe_4Na_2S_3.\end{array}\right.$$

The lixiviation is effected with warm water at 30° to 40°; the liquors yield after twenty-four to twenty-eight hours, without any previous concentration, a large crop of beautifully crystallised soda. The insoluble residue of the lixiviation is dried and roasted to produce sulphurous acid, employed in the manufacture of sulphuric acid, used in its turn for the conversion of common salt into sulphate of soda. Thus the cycle of changes in the sulphur is complete:—

$$\left.\begin{array}{l}Fe_4Na_2S_3\\14O\end{array}\right\}\text{ yield }\left\{\begin{array}{l}2Fe_2O_3\\Na_2SO_4\\2SO_2\end{array}\right.$$

The sulphate of soda present in the calcined residue is removed by lixiviation. It cannot be denied that this process presents certain advantages.

Direct Conversion of Common Salt into Soda. A plan for the direct conversion of common salt into soda has long been sought, but hitherto not successfully carried into practice. When a concentrated solution of bicarbonate of ammonia is mixed with strong brine, or, better still, the pulverised bicarbonate stirred through a concentrated solution of salt, and this mixture left to stand, the result will be that after some hours bicarbonate of soda will be deposited in crystalline state, the supernatant liquid being a solution of sal-ammoniac. As bicarbonate of soda on being gradually heated to redness loses a portion of its carbonic acid, and is converted into monocarbonate of soda, this process has been suggested as suited for the manufacture of soda, and has been tried by Dyar and Hemming in England. Schlœsing and Rolland in 1855 took out a patent for some improvements on this method of soda manufacture, of which the following is an outline:—The first operation consists in the action of ammonia and carbonic acid upon a concentrated salt solution; to 100 parts of water 30 to 33 parts of common salt, 8½ to 10 of ammonia, and carbonic acid in excess are taken. The next step is the separation of the bicarbonate of soda, which is effected by a centrifugal machine. The third stage is the calcination of the bicarbonate of soda in cylindrical iron vessels, the carbonic acid gas given off being collected. The fourth and fifth operations aim at the recovery of the carbonic acid and ammonia from the liquid drained from the bicarbonate of soda while in the centrifugal machine. The liquid is heated in a boiler, the result being the escape of the ammonia and carbonic acid, which are conducted to a cylinder filled with coke, through which a cold aqueous solution of carbonate of ammonia trickles, causing the condensation of the ammonia, the carbonic acid escaping into a gasholder. Next, milk of lime is added to the liquid, and the heating being continued, all the ammonia is expelled. Lastly, the clear supernatant liquid is evaporated to recover the common salt. According to Heeren's researches on this subject, this process is more suited for the preparation of bicarbonate of soda; it is stated, however, that the researches of Marguerite and Sourdival have resulted in improvements on this method which may in future lead to its being advantageously adopted in some localities for the manufacture of soda.

Soda from Cryolite. Cryolite ($Al_2Fl_6,6NaFl$) is largely employed for the manufacture of soda by decomposing the mineral by ignition with lime:—

$$\left.\begin{array}{l}\text{1 mol. of Cryolite}\\\text{6 mols. of Lime}\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{6 mols. of Fluoride of calcium.}\\\text{1 mol. of Aluminate of soda.}\end{array}\right.$$

This last compound being soluble in water is decomposed by carbonic acid, and alumina precipitated, soda remaining in solution. 100 kilos. of cryolite yield—

Dry caustic soda	44	kilos.
Calcined soda	75	,,
Crystallised carbonate of soda	203	,,
Bicarbonate of soda	119·5	,,

Bauxite (see under Alumina), on ignition with sulphate of soda and carbonaceous matter, yields in a similar manner soda and alumina.

Soda from Nitrate of Soda. By the conversion of nitrate of soda into nitrate of potassa by the aid of carbonate of potassa (see under Saltpetre) not inconsiderable quantities of a strong solution of soda are obtained; the sodium of the sodium nitrate may be converted by any of the following means into soda or caustic soda:—

a. By igniting nitrate of soda with carbonaceous matter.
b. By igniting nitrate of soda with silica, and decomposing the silicate of sodium by carbonic acid.
c. By igniting nitrate of soda with manganese.
d. By the decomposition of nitrate of soda.
  α. By means of carbonate of potassa; or,
  β. By means of caustic potassa.

In the latter case, besides nitrate of potassa, caustic soda is formed.

Caustic Soda. This substance, sodium hydroxide (NaHO), is met with in commerce as a highly concentrated solution, or more frequently as a solid mass, fused hydrate of soda, consisting in 100 parts of 77·5 parts of soda and 22·5 parts water. For many years a moderately strong solution of caustic soda was prepared by treating a carbonate of soda solution with caustic lime, but Dale was the first to use this solution instead of water in his boilers, and thus concentrate the lye to a sp. gr. of 1·24 to 1·25, after which the ley was further evaporated in cast-iron cauldrons to a sp. gr. of 1·9, at which point it solidifies on cooling.

Instead of using caustic lime, caustic soda is now directly produced by simply increasing the quantity of small coal added to the mixture of sulphate and chalk, the crude soda being at once lixiviated with water at 50°. After the liquor has cleared, it is rapidly concentrated to 1·5 sp. gr., when carbonate, sulphate, and chloride of sodium are deposited, the liquor assuming a brick-red colour, due to a peculiar compound of double sulphuret of sodium and sulphuret of iron. The ley is next strongly heated in large cast-iron cauldrons, and there is added 3 to 4 kilos. of Chili-saltpetre for every 100 kilos. of caustic soda required; by this operation the nitrate of soda reacts upon the sulphuret of sodium and cyanide of sodium present, causing an abundant evolution of ammonia and nitrogen. This somewhat complicated process may be elucidated by either of the two following formulæ:—

$$\alpha.\quad 2Na_2S + 2NaNO_3 + 4H_2O = 2Na_2SO_4 + 2NaHO + 2NH_3.$$

$$\beta.\quad 5Na_2S + 8NaNO_3 + 4H_2O = 5Na_2SO_4 + 8NaHO + 8N.$$

According to Pauli, the kind of reaction depends chiefly on the temperature of the heated ley; at 155° ammonia is largely evolved; above 155° and with greater concentration of the ley nitrogen is given off. As for every ton of caustic soda produced this process absorbs 0·75 to 1 cwt. of nitrate of soda, the ley is in some works oxidised by filtering it through a column of coke, or by forcing air through it in minute jets.

New Methods of Caustic Soda Manufacture. Among these is the decomposition of sulphate of soda by means of caustic baryta, a rather expensive process, baryta white or permanent white being a by-product. Unger uses caustic strontia instead of caustic baryta. Caustic soda may be prepared by treating cryolite for sulphate of alumina (see Alum), or by igniting nitrate of soda with manganese; or by decomposing silico-fluoride of sodium or fluoride of sodium with caustic lime. In England very pure caustic soda is prepared from sodium by carefully oxidising the metal with pure water in bright iron or silver vessels.

According to Dalton's researches :—

A caustic soda liquor of the undermentioned sp. gr.	Contains percentage of caustic soda (NaHO.)
2·00	77·8
1·85	63·6
1·72	53·
1·63	46·6
1·56	41·2
1·50	36·8
1·47	34·0
1·44	31·0
1·40	29·0
1·36	26·0
1·32	23·0
1·29	19·0
1·23	16·0
1·18	13·0
1·12	9·0
1·06	4·7

Caustic soda is largely used in soap-making, paraffin and petroleum refining, and the preparation of silicate of soda and artificial stone by Ransome and Sims's method.

Bicarbonate of Soda. This substance, $NaHCO_3$, called erroneously carbonate of soda in many of the London shops, consists in 100 parts of 36·9 soda, 10·73 water, and 52·37 carbonic acid, and is prepared by passing a current of washed carbonic acid gas through a solution of carbonate of soda. If the solution is concentrated the bicarbonate is deposited as a powder, but from a dilute solution large crystals are obtained. It is, however, more advantageous to cause the carbonic acid to act upon crystallised and effloresced carbonate of soda; a suitable mixture consists of 1 part of crystallised and 4 parts of effloresced carbonate of soda. The sources of carbonic acid may differ, but in this country the gas is generally prepared by the action of weak hydrochloric acid upon chalk or limestone; of course the carbonic acid evolved during the fermentation of wort, or must, may be applied.

When carbonic acts upon crystallised carbonate of soda there is first formed sesquicarbonate of soda; the 9 equivalents of water which are displaced from each equivalent of crystallised carbonate of soda are collected in a reservoir, and this liquid having of course dissolved a portion of the bicarbonate is employed at a future operation for moistening the crystallised soda carbonate. The bicarbonate is dried at 40° in a current of carbonic acid gas. The preparation of the bicarbonate by withdrawing from the monocarbonate by the aid of an acid one-half of the soda it contains has been suggested; for this purpose $28\frac{1}{2}$ parts of crystallised sodic carbonate are dissolved in twice their weight of warm water, and $4\frac{9}{13}$ parts of sulphuric acid added, care being taken not to move the vessel. Being left to stand for several days the bicarbonate is deposited in crystals. It has been seen that when a solution of common salt is treated with bicarbonate of ammonia, the result is the formation of bicarbonate of soda and sal-ammoniac, which remains in solution. Bicarbonate of soda crystallises in monoclinical, tabular crystals; has a weak alkaline reaction; loses its carbonic acid at 70°, and becomes monocarbonate of soda; and by exposure to dry air is gradually converted into sesquicarbonate. The bicarbonate is employed generally in the preparation of effervescing drinks, and with hydrochloric or phosphoric acid in making bread without fermentation. The further uses of this salt are—the precipitation of the alumina from sodium-aluminate solutions, for the preparation of baths, for gilding and platinising, and for purifying and cleansing silk and wool. 1 grm. of the bicarbonate yields, when completely decomposed by an acid, about 270 c.c. of carbonic acid gas = 0·52 grm. by weight.

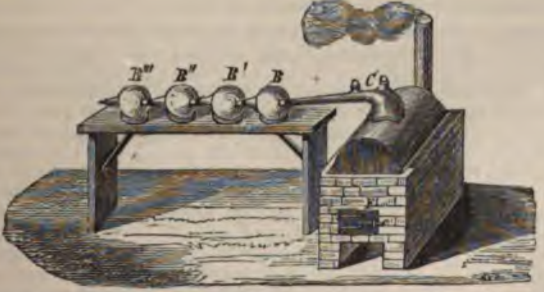
The total production of soda in Europe amounted in 1870 to 11,850,000 cwts., of which Great Britain produced 6,250,000 cwts.

PREPARATION OF IODINE AND BROMINE.

Preparation of Iodine. This element occurs in sea-water, from which it is taken up by various sea-weeds; from these sea-weeds iodine is derived industrially. Chili-saltpetre and some saline springs (for instance, the Sulza, Sadiem Weimar) contain iodine in considerable quantity. Although iodine is found in the mineral kingdom (for instance, in the iodide of lead and phosphorites of Amberg, Bavaria, and Diez on the Lahn), it is not in this case industrially important. The chief seat of iodine manufacture is at Glasgow, where there are twelve factories; there are two iodine factories in Ireland, and two at Brest, in France.

Preparation from Kelp. In order to obtain iodine from sea-weeds, the latter are first converted into kelp, that is to say, they are incinerated, the product broken to pieces and lixiviated with water, leaving an insoluble residue of 30 to 40 per cent., and yielding to the liquid 60 to 70 per cent. This solution, having a sp. gr. of 1·18 to 1·20, contains chlorides, sulphates, and carbonates of alkalies, sulphuret of potassium, iodide of potassium, and hyposulphites of alkalies; by evaporating and cooling the liquor, the sulphate of potassa and chlorides of potassium and sodium are removed. To the remaining mother-liquor, previously poured into shallow open vessels, dilute sulphuric acid is added, the result being, that while a strong evolution of gases, sulphuretted hydrogen, and carbonic acid takes place, there is formed a thick scum and a deposit of sulphur at the bottom of the vessel; the sulphur when washed and dried is sold. When the evolution of gas has completely ceased, more sulphuric acid is added, and, according to Wollaston's method, the required quantity of manganese; this mixture is poured into a large leaden distilling apparatus, C, Fig. 85. By this means the iodine is set free, carried over in the state of vapour to the receivers, B, B′, B″, and condensed as a solid crystalline mass. In Paterson's large iodine works at Glasgow this operation is carried on in a cast-iron hemispherical vessel of 1·3 metres diameter, the cover

FIG. 85.



being a leaden dome, to which are fitted two earthenware stillheads, connected by means of porcelain tubing with two earthenware receivers, Fig. 85, each consisting of 4 to 5 parts. At Cherbourg, iodine is obtained, according to Barruel's plan, by passing chlorine gas into the mother-liquor; by this plan the iodine is separated from the iodide of magnesium, the latter taking up chlorine instead—

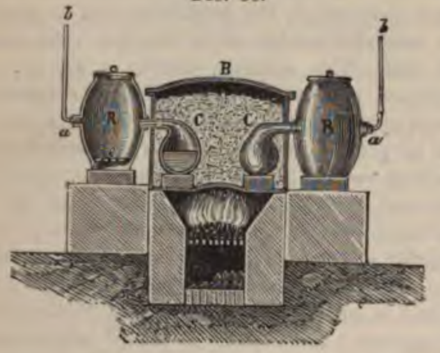
$$(MgI_2 + Cl_2 = MgCl_2 + I_2).$$

A more recent method, by which all the iodine present in the mother-liquor is obtained, consists in distilling the liquor with chloride of iron—

$$(2NaI + Fe_2Cl_6 = 2I + 2NaCl + 2FeCl_2).$$

As iodine is only very slightly soluble in water, 1 part of iodine requiring 5524 parts of water at 10° to 12° for its solution, that is, 1 grain of iodine to 12 ounces of water, it is carried over with the steam and deposited at the bottom of the receiver in the form of a black powder. When iodine is prepared by the aid of chlorine, the quantity of gas should be exactly sufficient to decompose the iodide of magnesium, for if the quantity of chlorine be too small no iodine is separated, and if too large chloride of iodine is formed and free bromine, both of which being volatile escape. The iodine when removed from the receivers is drained on porous bricks or tiles, and dried between folds of blotting-paper. It need hardly be said that the iodine should not come in contact with a metallic surface. The iodine thus obtained has to be purified by sublimation, an operation carried on in the apparatus represented in Fig. 86, consisting of stoneware retorts, C C, placed in the sand-bath, B, heated as shown in the woodcut. Each of these retorts is filled with upwards of 40 lbs. of crude iodine, and entirely surrounded by sand, in order to prevent the sublimation of any iodine in the necks of the retorts. These are then connected with the receiver or condenser, R R, in which the crystalline iodine is deposited, the tubes, *a b*, *a b*, being for the purpose of carrying off the watery vapour. 1 ton of kelp yields on an average 4·07 kilos. of iodine.

FIG. 86.



Stanford and Moride's Method of Preparing Iodine from Carbonised Sea-weed. In 1862, Mr. Stanford suggested that the sea-weeds should not be calcined, but simply distilled with superheated steam, so as to prevent volatilisation of the iodine, while the tarry and gaseous products should be separately utilised. This carbonised sea-weed, when quite cold, is lixiviated with water, and the solution treated for iodine and chloride of potassium (see p. 130). The volatile products of the distillation are illuminating gas, acetic acid, ammonia, mineral oil, and paraffin. M. Moride, of Nantes, has modified this process: he prepares by evaporating the liquor from the lixiviation of the carbonised sea-weed, sulphate and chloride of potassium, &c. The mother-liquor is treated with chlorine or hyponitric acid, and then with benzine, in an apparatus so arranged that the benzine directly gives up the iodine it has dissolved to soda or potassa, the benzine thus acting as a continuous solvent. The liquor containing iodine is treated for the separation of iodine in the usual manner.

Preparation of Iodine from Chili-Saltpetre. Crude Chili-saltpetre contains on an average 0·059 to 0·175 per cent. of iodine. According to Nöllner, the iodine occurs from the formation of the Chili-saltpetre in the presence of decaying sea-weeds from shallow, stagnant, inland seas, which have dried up. The mother-liquors, left after the refining of the salt, or from its use for the conversion of chloride of potassium into nitrate of potassa, and containing 0·28 to 0·36 per cent. of iodine, are treated with sulphurous acid until the iodine separated begins to re-dissolve. More recently nitrous acid has been used instead of sulphurous acid. The iodine thus obtained is refined by sublimation, while that remaining in the residual saline matter is removed by a further treatment with chlorine.

Properties and Uses of Iodine. Iodine ($I = 127$; Sp. gr. $= 4{\cdot}94$) is a black-grey coloured crystalline substance, with a metallic appearance not unlike graphite. On being heated iodine is converted into vapours, which, according to Stas, when concentrated exhibit a blue colour, and a violet in a more dilute state. Iodine fuses at 115°, and boils above 200°. It is somewhat soluble in water, readily so in alcohol, ether, hydriodic acid, iodide of potassium solution, sulphide of carbon, chloroform, benzol, aqueous solution of sulphurous acid, and solution of hyposulphite of soda. A solution of iodine imparts a violet colour to starch. Adulteration of iodine with either pulverised charcoal or graphite may be at once detected by treating a sample with alcohol or a solution of hyposulphite of soda, in each of which the iodine, if pure, ought to dissolve completely, leaving no residue on sublimation. Sometimes the weight of iodine is fraudulently increased by the addition of water. Iodine is largely used in photography combined as iodide of potassium; for the preparation of other iodine compounds, for instance, iodide of mercury; also in the preparation of some of the tar colours, iodine violet, iodine green, and cyanine blue, the latter a compound from iodine and lepidin, a volatile base. The total production of iodine in Europe and Chili amounted in 1869 to 3453 cwts., more than half, or 1829 cwts., being produced in Scotland and Ireland.

Preparation of Bromine. The element known as bromine occurs to a small extent in sea-water, a litre containing 0·061 grms. bromine. The mother-liquors, however, of many salt works (for instance, those at Schönebeck, near Magdeburg, and the liquors left from many of the Stassfurt salts) are so rich in bromine, that its preparation is worth the cost and trouble. In order to avoid as much as possible the admixture of chlorine, there is added to the mother-liquor dilute sulphuric acid; this mixture is heated to 120°, and the hydrochloric acid set free by the sulphuric acid evolved, while the less volatile hydrobromic acid is left in the liquor, from which, on cooling, sulphates are deposited. The decanted liquor is distilled after the addition of more sulphuric acid and some manganese. Two Woulfe's bottles serve as receivers; in the first are condensed water, bromine, bromoform, and bromide of carbon, while any bromine vapours which pass over to the second bottle are absorbed in the caustic soda it contains. The ley contained in this vessel is evaporated to dryness, the residue ignited in order to convert bromate of soda into bromide of sodium; the saline mass being then mixed with sulphuric acid and manganese and distilled, yields pure bromine, best preserved under strong sulphuric acid.

According to Leisler's patent (1866) bromine is separated from the mother-liquor left by operations with kainite, or carnallite, or from the water of the Dead Sea (containing, according to Lartet's analysis, in 1 litre, taken from a depth of 300 metres, 7·093 grms. $= 0{\cdot}7$ per cent. of bromine) by adding bichromate of potassa and an acid; heat being applied, the bromine is volatilised and collected in a condenser filled with metallic iron. From the bromide of iron thus formed, either the element itself or any of its compounds may be obtained. The apparatus employed by this patentee is a distilling apparatus; the acid is hydrochloric diluted with four times its bulk of water; to 100 parts by bulk of the bromine fluid, 1 part by bulk of acid is added. The bichromate is added in a saturated aqueous solution. The bromide of iron formed becomes dissolved by the aqueous vapour, and condensed in the receiver. Bromine is the only metalloid fluid at ordinary temperature. Seen in thick layers its colour is a deep brown-red, but in thin layers a hyacinth-red; its odour is strong and similar to that of chlorine gas. The aqueous solution of bromine—1 part requiring 30 parts of water for its solution—is of a yellow-red colour when freshly made, but like chlorine-water does not keep well, and is soon converted, especially if exposed to light, into a colourless solution of weak hydrobromic acid. 100 parts of bromine water contain at 15°, 3·226 parts of bromine; bromine forms with water a solid hydrate at 0°. It is readily soluble in ether, alcohol, chloroform, and hydrobromic acid. It yields with an aqueous solution of sulphurous acid hydrobromic acid—

$$(SO_2 + H_2O + 2Br = SO_3 + 2BrH).$$

Bromine boils at 63°, giving off deep red vapours; at −7·3° it becomes a lead-grey coloured, foliated, graphite-like mass. Bromine acts upon colouring matters, dyes, and the colours of flowers as does chlorine, while organic matters, especially those of animal origin, are coloured brown. It is used in combination as bromides of potassium, ammonium, cadmium, and hypobromite of potassa, for photographic purposes and in medicine; and further as bromides of ethyl, amyl, and methyl, for the preparation of some of the tar colours, Hofmann's blue, and the preparation of alizarine from anthracen. Bromine is also used as a disinfectant, and, according to Reichardt, may with advantage be substituted for chlorine in the preparation of ferricyanide of potassium. Since the year 1866 bromine has been manufactured at Stassfurt, now the chief bromine-producing locality. The total annual production of bromine in Europe and America amounts to 1150 cwts., of which 400 cwts. are obtained at Stassfurt, and 300 cwts. in Scotland.

SULPHUR.

Sulphur. In combination with coals, rock-salt, and iron, sulphur is the mainstay of present industrial chemistry. It is often found native between gypsum, clay, and marl in tertiary deposits, more rarely in veins between crystalline rocks of the schistose and metamorphic varieties, and not unfrequently in coal and lignite deposits. Sulphur is an almost constant product of active volcanoes, being sublimed and deposited on surrounding objects. The largest sulphur deposits in Europe are met with in Sicily. It is also found in Egypt on the banks of the Red Sea, especially near Suez; at Corfu, one of the Ionian Islands; near the Clear or Borax Lake in California; on the slopes of the Popocatepetl, in the province of Puebla, Mexico, where yearly 2000 cwts. of sulphur are collected. Frequently, sulphur is deposited from the sulphuretted waters of mineral springs; for instance, the waters of Aix-la-Chapelle. Sulphur occurs in combination with metals, as in iron pyrites, FeS_2, with 53·3 per cent. of sulphur; this mineral often contains thallium. The quantity of sulphur contained in the following minerals is, from 100 parts:—Iron pyrites (FeS_2), 53·3; copper pyrites ($Fe_2Cu_6S_6$), 34·9; magnetic iron pyrites, mundic (Fe_7S_8, or, according to Th. Petersen, FeS), 39·5; galena (PbS), 13·45; black-jack (ZnS), 33·0; kieserite ($MgSO_4 + H_2O$), 23·5; anhydrite ($CaSO_4$), 23·5; gypsum ($CaSO_4 + 2H_2O$), 18·6; gas coal, 1·0. According to Dr. Wagner, the quantity of sulphur present in the coals used in the London gasworks annually, amounts to 200,000 cwts., equal to 612,500 cwts. of sulphuric acid.

Although sulphur occurs native as sulphuretted hydrogen and sulphurous acid, especially near active volcanoes, this is not of much industrial use. The regeneration of sulphur from soda-waste is decidedly one of the most important items in the sulphur industry.

Smelting and Refining Sulphur. According to the comparative richness of the raw material, the sulphur is separated from its concomitant impurities by melting or by distillation. When the raw material is rather rich it is simply submitted to a process of melting in a cast-iron cauldron, B (Fig. 87), heated by a gentle coal or charcoal fire placed in A. During the melting the mass is stirred with an iron rod, and as soon as the sulphur has become quite fluid, the gangue and small stones are removed by means of the ladle, C. This done, the sulphur is poured into a wooden or sheet-iron vessel D, thoroughly wetted with water to prevent the adhesion of the sulphur to the sides. The sulphur when cold and solid is broken into large lumps and packed in casks ready for the market. The stones and gangue are placed in heaps, or more commonly introduced into a shaft furnace (Fig. 88), and, a portion of the sulphur being sacrificed to serve as fuel, the greater part of the element is eliminated by the following plan:—A small portion of the crude sulphur is ignited in the lower part of the furnace, and the shaft, E, filled with large lumps of the earthy sulphur ore, from which, rapidly ignited superficially, the molten sulphur trickles down. The openings, *f f f*, give access to the air required for the combustion of a portion of the sulphur. The sulphur collects in the lower part of the furnace and is tapped off by the channel *g* into wooden or sheet-iron vessels. A far better method of preparing sulphur from the ore is by distillation, the apparatus being that exhibited in Fig. 89. A is a cast-iron cauldron, which is filled with raw material, and covered with a tightly-fitting iron lid. The flues are so constructed as to heat the vessel D gently. The vapours of sulphur are carried by the tube *m* into the condenser, B, whence the molten sulphur runs off into the vessel *k*. The previously warmed ore is readily admitted to A by lifting the damper, *p*. From a suggestion made by E. and P. Thomas, sulphur is obtained from its ores by the application of superheated steam at 130°, this mode of working being the same as that employed by M. Schaffner for purifying the sulphur recovered from soda-waste. In passing, it may be mentioned that very recently the extraction of sulphur from its ores has been attempted

Fig. 87.

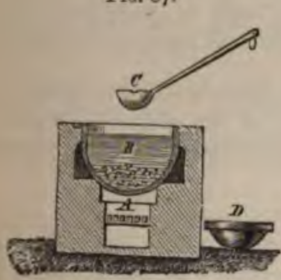


Fig. 88.

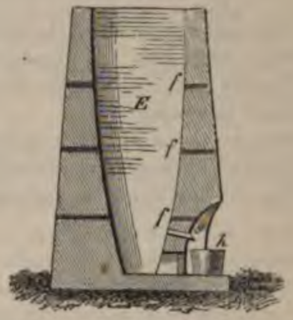
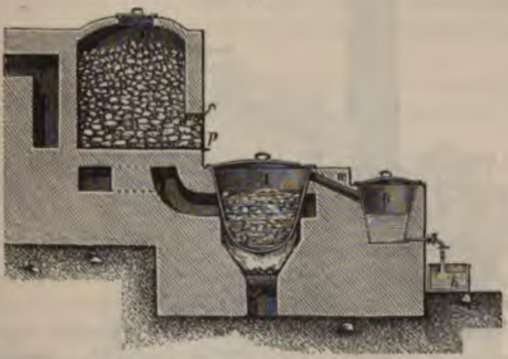


Fig. 89.



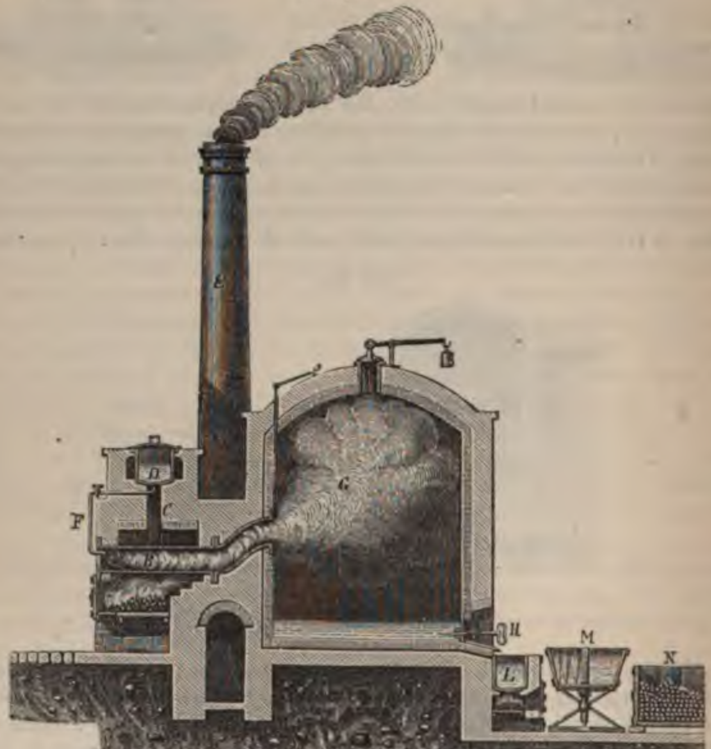
by the aid of solvents, viz., sulphide of carbon and a light coal-tar oil of sp. gr. = 0·88. M. Mène's analyses of several samples of crude Sicilian sulphur obtained by smelting are—

	1.	2.	3.	4.	5.
Sulphur (soluble in CS_2)	90·1	96·2	91·3	90·0	88·7
Carbonaceous matter	1·0	0·5	0·7	1·1	1·0
Sulphur (insoluble in CS_2) ..	2·0	—	1·5	2·1	1·7
Siliceous sand	2·3	1·5	3·3	2·8	5·5
Limestone (sometimes cœlestin)	4·1	1·8	2·5	3·0	2·8
Loss	0·5	—	0·7	1·0	0·3

The bottom portion of the blocks of crude sulphur often contains 25 per cent. of foreign substances. The crude sulphur is refined in order to eliminate all traces of earthy matter; and after this process it is brought into commerce in sticks or rolls or in powder.

Lamy's Refining Apparatus. The apparatus for refining sulphur, invented by Michel and improved by Lamy, at Marseilles, consists mainly of two cast-iron cylinders, B (Fig. 90), used as retorts, and a large brick-work condensing-room, G. The cylinder B

Fig. 90.



is directly heated by the fire, the smoke of which is carried off by the chimney, E. The flues, C, however, surround D, where the crude sulphur undergoes a partial refining, and whence it flows by the tube F into the cylinder B. The cylinder B is in communication with the vaulted room G. At the bottom of this room is placed a cast-iron plate in which a hole is bored, and fitted with a conical plug, J, connected with a rod, H, so as to admit of being shut and opened for the purpose of tapping sulphur into the cauldron, L, whence it is ladled over into the moulds placed in M. N is a box for the roll sulphur when it has become cold.

Roll Sulphur. If it is intended to prepare roll-sulphur, the mode of proceeding is the following:—Each of the cylinders is filled with crude sulphur, the lids firmly fastened, and the joints luted. Heat is at first applied to only one of the cylinders, and not until half of its contents are distilled off is the second cylinder heated. Gradually the heat at D increases to such an extent as to melt the crude sulphur; by this fusion the heavier earthy impurities settle down, while any moisture present is driven off. When the distillation of the contents of the cylinder first heated is finished, that cylinder is filled with liquid sulphur from D by means of the tube F. The quantity of sulphur treated in twenty-four hours yields 1800 kilos. pure material collected in G. The temperature of this room being 112°, the sulphur is there kept in a molten state, and as soon as a sufficient quantity has collected at the bottom, it is tapped off into L, and cast in the moulds. When it is desired to prepare flowers of sulphur, the mode of operation is the same, but the temperature of G should be kept at or rather below 110°. This is effected by making the distillation interrupted instead of continuous, so that in twenty-four hours there are only two distillations of 150 kilos. each. As soon as a sufficient quantity of flowers of sulphur has been condensed in the room G, the door of the room is opened and the sulphur removed.

Flowers of Sulphur.

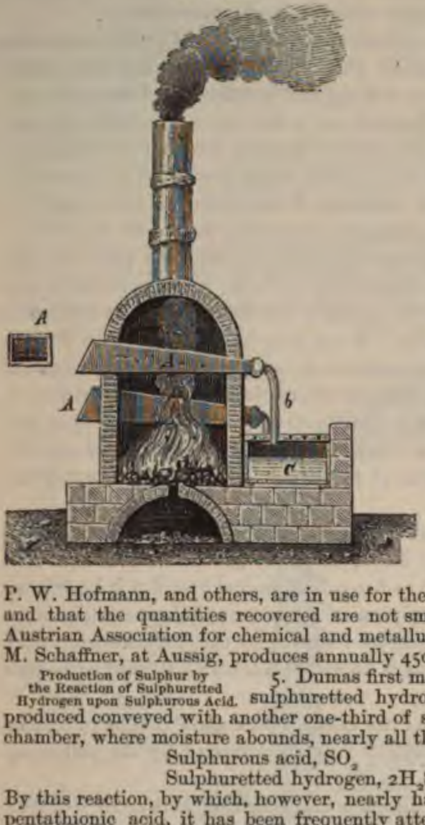
Dujardin improved upon this apparatus in 1854. By this process of distillation of sulphur a loss of 11 to 20 per cent. is incurred, partly due to combustion of a portion of the sulphur. The residue left in the cylinders and vessel D is known as sulphur-slag. The ordinary flowers of sulphur of commerce always contain some sulphuric and sulphurous acids, which can be removed by carefully washing with water. Sulphur so treated and gently dried is known in pharmacy as washed flowers of sulphur, *Flores sulphuris loti.*

Preparation of Sulphur from Pyrites. Where fuel and labour are cheap, and a good quality of iron or other pyrites is found in abundance, sulphur may be prepared by the following process:—

1. From iron pyrites, FeS_2. As this mineral consists in 100 parts of 46·7 of iron and 53·3 of sulphur, it is clear that if half of the latter be removed by distillation, there will be left a compound of iron and sulphur yielding green copperas after oxidation. Accordingly iron pyrites might by distillation lose 26·65 parts of sulphur, and the residue still be fit for making green copperas; but if this quantity were to be driven off in practice, the temperature would require to be raised so high as to melt the remaining monosulphuret and lead to the destruction of the fire-clay cylinders. The quantity of sulphur actually distilled off on the large scale is only 13 to 14 per cent., leaving a pulverulent residue which does not attack the fire-clay cylinders.

The process thus briefly outlined is carried on in the following manner:—The pyrites is put into conical fire-clay vessels, A A, Fig. 91, placed in a somewhat slanting position in the furnace; the lower and narrower portion of these vessels is fitted with a perforated diaphragm preventing any pyrites falling down *b*, while the volatilised or fluid sulphur can pass readily through the holes into a receiver, c, filled with water. After the vessels A A have been filled with pyrites, the fire is kindled and the distillation set in progress. The sulphur collected in the receiver has a grey-green colour, and is purified by being re-melted, after which it is sent into the market in coarsely broken up lumps. In order to free this kind of sulphur from sulphuret of arsenic, it is submitted to distillation, the residue being used in veterinary practice. The dark colour of the sulphur obtained from pyrites is due to an admixture of thallium far more than to the presence of arsenic. Mr. W. Crookes found in the sulphur obtained from Spanish pyrites as much as 0·29 per cent. of thallium.

FIG. 91.



Preparation of Sulphur by Roasting Copper Pyrites. 2. Sulphur may be obtained by the roasting of copper pyrites, and in this way becomes a by-product of smelting copper ores. Formerly this operation was carried on in peculiarly constructed furnaces in the copper-smelting works of the Lower Hartz, Germany; at the present time sulphur from this source is only obtained at Agordo in Italy, Wicklow in Ireland, and at Mühlbach, Salzburg, Austria.

Sulphur obtained as a By-Product of Gas Manufacture. 3. Since Laming's mixture has been employed in purifying coal-gas, sulphur has to some extent been obtained as a by-product. Laming's mixture is hydrated, or any soft porous peroxide of iron mixed with sawdust; and in this mixture sulphur may accumulate to upwards of 40 per cent. ($Fe_2O_3 + H_2S = 2FeO + H_2O + S$). According to Hill's patent the sulphuret of iron is calcined to obtain sulphurous acid, which is employed in the preparation of sulphuric acid.

Sulphur from Soda Waste. 4. We have already seen, while treating of the manufacture of soda (*vide* p. 185) that several processes due to MM. Schaffner, Guckelberger, Mond, P. W. Hofmann, and others, are in use for the regeneration of sulphur from soda waste; and that the quantities recovered are not small may be inferred from the fact that the Austrian Association for chemical and metallurgical products, under the management of M. Schaffner, at Aussig, produces annually 450,000 kilos. of sulphur in this manner.

Production of Sulphur by the Reaction of Sulphuretted Hydrogen upon Sulphurous Acid. 5. Dumas first made the observation that when one-third of sulphuretted hydrogen is burned off, and the sulphurous acid produced conveyed with another one-third of sulphuretted hydrogen into a leaden or brick chamber, where moisture abounds, nearly all the sulphur is regenerated:—

$$\left.\begin{array}{l}\text{Sulphurous acid, } SO_2 \\ \text{Sulphuretted hydrogen, } 2H_2S\end{array}\right\} \text{yield} \left\{\begin{array}{l}\text{Sulphur, } 3S. \\ \text{Water, } 2H_2O.\end{array}\right.$$

By this reaction, by which, however, nearly half the sulphur is lost in the formation of pentathionic acid, it has been frequently attempted to obtain sulphur from gypsum, heavy spar, and soda waste. The process is briefly as follows:—For instance, heavy spar, native sulphate of baryta, is reduced to sulphuret of barium, which is treated with hydrochloric acid, sulphuretted hydrogen and chloride of barium of course being formed. Either a portion of the gas is burnt and to the products of the combustion, sulphurous acid and water, the rest of the gas added, or the sulphuretted hydrogen is conveyed into water to which sulphurous acid is simultaneously conveyed from the combustion or roasting of iron pyrites. Mr. Gossage long since proved that, by conveying sulphuretted hydrogen into chloride of iron, the sulphur of the gas is deposited. Sulphur may be obtained by a similar reaction as a by-product of the manufacture of iodine and potassa salts from kelp. At Paterson's iodine factory at Glasgow, 2000 cwts. of this sulphur are obtained annually. According to E. Kopp the incomplete combustion of sulphuretted hydrogen yields sulphur economically ($H_2S + O = H_2O + S$).

Sulphur obtained by the Reaction of Sulphurous Acid on Charcoal. 6. When sulphurous acid gas is conveyed over red-hot charcoal, the latter is converted into carbonic acid, while sulphur is set free. By this reaction the sulphurous acid from the roasting of zinc ores (black-jack) is converted into sulphur in large quantities at Borbeck, near Essen, Prussia.

By Heating of Sulphuretted Hydrogen. 7. When sulphuretted hydrogen is passed through red-hot tubes it is decomposed; but this reaction is not industrially applicable to the preparation of sulphur.

Properties and Uses of Sulphur. The yellow colour of sulphur is generally known; at 100° this colour deepens and nearly disappears. At −50°, sulphur is very brittle and readily pulverised, becoming by the friction, especially in warm and dry weather, so highly electric as to cause the particles to adhere strongly to each other. The sp. gr. of this element varies from 1·98 to 2·06. It melts at 115°, forming a thin yellow liquid, which, at 160°, becomes thick and assumes an orange-yellow colour; when heated to 220°, sulphur is a tough, red, semi-solid; between 240° and 260° the colour becomes red-brown, but being heated above 340° the sulphur is again somewhat fluid, and at last boils at 420° without having lost its deep colour, which also characterises the vapours. When sulphur heated to 230° is suddenly poured into cold water, it remains soft and so plastic that it may be advantageously employed for obtaining impressions of medals, woodcuts, and engraved plates, these impressions, as the sulphur again hardens after a few days, serving as moulds. On being heated in contact with air, sulphur burns, forming sulphurous acid. It is insoluble in water, very slightly soluble in absolute alcohol and ether, and rather more soluble in warm fixed and volatile oils, forming the so-called sulphur balsam. The best solvents for sulphur are—sulphide of carbon, coal-tar oil, benzol, and chloride of sulphur.* It also dissolves in boiling solutions of caustic soda or potassa, in hot solutions of sulphurets of calcium and potassium, in the solutions of certain sulpho-salts; for instance, the compound Sb_2S_3,Na_2S, which is converted into Sb_2S_5,Na_2S, and in solutions of alkaline sulphites, converted thereby into hyposulphites.

Sulphur is used in the manufacture of sulphuric acid, gunpowder, fireworks, for sulphuring hops and vines as a preservative against some diseases of these plants; the quantity of sulphur used for the purpose of sulphuring vines in France, Spain, and Italy, amounted, in 1863, to 850,000 cwts. of Sicilian sulphur, being about from 20 to 25 per cent. of the entire production. It is further employed in the manufacture of sulphurous acid, sulphites, and hyposulphites, sulphide of carbon, cinnabar, mosaic gold or bisulphide of tin, and other metallic sulphurets, ultramarine, various cements, and for vulcanising and ebonising india-rubber and gutta-percha.

The greater part of the total sulphur production of Europe comes from Sicily, whence, in 1868, 4,052,000 cwts., in value about £1,500,000, were exported. The total sulphur production in Europe in 1870 amounted to 7,012,500 cwts., but in this quantity the sulphur recovered from soda waste is not included.

SULPHUROUS AND HYPOSULPHUROUS ACIDS.

Sulphurous Acid. This acid (SO_2, or hydrated H_2SO_3) may be obtained—

a. By oxidation of sulphur;

b. By reduction of sulphuric acid;

c. By a combination of the processes *a* and *b*.

The preparation of sulphurous acid by the oxidation of sulphur may be—*a*. By burning brimstone in the air; *β*. By roasting or calcining iron and copper pyrites, or the product of Laming's mixture from the purifiers of gas-works; *γ*. By igniting a mixture of manganese and sulphur. The preparation of sulphurous acid by roasting sulphurets when coupled with metallurgical operations, is, especially since Gerstenhöfer's furnace has been more generally introduced, the most advantageous plan of obtaining this acid, and also where the acid is required for the manufacture of sulphuric acid. When, however, sulphurous acid is required for the purpose of preserving food, and as a raw material in the preparation of wines, hops, &c., it should not be

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* According to Cossa (1868)—

100	parts of	sulphide of	carbon	dissolve at	15·0°	31·15	parts of	sulphur.
100	„	„	„	„	38·0°	94·57	„	„
100	„	„	„	„	48·5°	146·21	„	„
100	„	benzol	„	„	26·0°	0·96	„	„
100	„	„	„	„	71·0°	4·37	„	„
100	„	ether	„	„	23·5°	0·97	„	„
100	„	chloroform	„	„	22·0°	1·20	„	„
100	„	aniline	„	„	130·0°	85·27	„	„

According to Pelouze—

100 parts of coal-tar oil, sp. gr. 0·88, dissolve, at 130·0°, 43·0 parts of sulphur.

made from pyrites, but from sulphur, as, when obtained from pyrites, it is always mixed with arsenious acid. The Laming's mixture saturated with sulphur from gas-works is largely used in the preparation of sulphurous acid in sulphuric acid works in and around London. The ignition in close vessels of metallic oxides and sulphur can only be advantageously used for the preparation of sulphurous acid under certain conditions. The oxides chiefly used for this purpose are those of manganese and copper; the former yields, according to the weight of the materials employed, either only half the weight of the sulphur in the shape of sulphurous acid, or the whole of the sulphur may be converted into acid. Sulphurous acid is sometimes prepared by heating a mixture of sulphate of iron and sulphur—

$$FeSO_4 + 2S = FeS + 2SO_2).$$

When sulphate of zinc is calcined it yields sulphurous acid and oxygen—

$$(ZnSO_4 = SO_2 + O + ZnO).$$

Kieserite ($MgSO_4 + H_2O$), mixed with charcoal yields all its sulphuric acid as sulphurous acid.

The preparation of sulphurous acid by the reduction of sulphuric acid is very frequent; sulphuric acid is reduced by being strongly heated in contact with certain metals; for instance, copper, mercury, and silver:—

$$\left.\begin{array}{l}\text{Sulphuric acid, } 2H_2SO_4\\ \text{Copper, } Cu\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Sulphate of copper, } CuSO_4,\\ \text{Sulphurous acid, } SO_2,\\ \text{Water, } 2H_2O.\end{array}\right.$$

A small quantity of sulphuret of copper is also formed. The dilution of sulphurous acid with carbonic acid and carbonic oxide does not interfere with its intended use. Sulphuric acid is decomposed and reduced by being boiled with charcoal-dust, sawdust, wood-shavings, &c.

$$\left.\begin{array}{l}\text{Sulphuric acid, } 2\,H_2SO_4\\ \text{Charcoal, } C\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Sulphurous acid, } 2SO_2,\\ \text{Carbonic acid, } CO_2,\\ \text{Water, } 2H_2O.\end{array}\right.$$

This mode of operation may be made continuous by keeping up a supply of sulphuric acid and sawdust in the glass retort, as the decomposition of both these substances is complete, yielding sulphurous acid, water, and carbonic acid. When the vapours of sulphuric acid are passed through red-hot glass or porcelain tubes, the result is the formation of sulphurous acid, oxygen, and water ($H_2SO_4 = SO_2 + O + H_2O$). The reduction and decomposition of sulphuric acid by the aid of sulphur may be viewed as a combined process of preparing sulphurous acid by oxidation and reduction:—

$$\left.\begin{array}{l}\text{Sulphuric acid, } 2H_2SO_4\\ \text{Sulphur, } S\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Sulphurous acid, } 3SO_2,\\ \text{Water, } 2H_2O.\end{array}\right.$$

In practice, however, this operation is very difficult, owing to the fact that, long before the reaction begins to take place, the sulphur is molten, while as soon as the reaction sets in it becomes very tumultuous, and with the sulphurous acid gas vapours of sulphur are carried over, which solidify and obstruct the passage. At the ordinary temperature and pressure of the atmosphere, sulphurous acid is a gas having a pungent odour, and a sp. gr. = 2·21. This gas dissolves readily and in large quantity in water, 1 volume absorbing at 18°, 44 volumes of gas. It is even more soluble in alcohol. When water is present all the higher oxides of nitrogen give up some of their oxygen to the sulphurous acid, converting it into sulphuric acid, the oxides forming deutoxide of nitrogen. Chlorine also converts moist sulphurous acid gas into sulphuric acid, and similar results obtain with iodine. The mixture of sulphurous acid and sulphuretted hydrogen causes their mutual decomposition, water being formed, and sulphur deposited. Sulphurous acid is chiefly employed in preparing sulphuric acid, in the manufacture of paper, as so-called antichlorine, in the preparation of madder by E. Kopp's process, the preparation of hyposulphite of soda, and the manufacture of sulphate of ammonia from lant (stale urine). Sulphurous acid is employed according to Laminne's patent for the purpose of decomposing alum-shale in the manufacture of alum.

It is further employed in some metallurgical processes, for preserving food, bleaching syrups, silk, wool, sponges, feathers, glue, isinglass, and other animal substances, which do not admit of being treated with chlorine, and for bleaching straw hats, willow and wicker baskets, gum arabic, &c. The bleaching property of sulphurous acid may be considered as due to two entirely different causes: in some instances the pigment is only masked, not destroyed, as sulphurous acid enters with some pigments into a colourless combination; in other instances, however, a real decomposition of the pigment takes place. The former condition obtains with most of the blue and red flowers and fruits; a red rose bleached by sulphurous acid has its colour restored by immersion in very dilute sulphuric acid. The pigments of yellow flowers are not affected by sulphurous acid; it also does not at first act upon indigo and carmine and the yellow colour of raw silk, but by the combined and continued action of this acid and direct sunlight, the oxygen of the acid acts as ozone and determines the bleaching. The avidity of sulphurous acid for oxygen may be utilised in extinguishing fires, especially in the case of the soot of chimneys catching fire, which may be very readily subdued by throwing a few ounces of flowers of sulphur into the fireplace or stove.

Sulphite of Lime. Neutral sulphite of lime ($SCa_2O_3 + H_2O$), containing in 100 parts 41 parts of sulphurous acid, deserves attention as a cheap, commodious, and very efficient substance for the development of sulphurous acid, the gas being readily set free by the action of hydrochloric or sulphuric acid. Bisulphites of lime and soda, the former in solution, the latter as a solid dry powder, are largely produced in some of the beet-root sugar manufacturing countries.

Hyposulphite of Soda. This salt ($S_2Na_2O_3 + 5H_2O$) is largely used in photography, in metallurgy, as a mordant in calico-printing, and as antichlor in paper-making. Hyposulphite of soda may be prepared by several methods. According to Anthon, 4 parts of calcined sulphate of soda are mixed with 1 to 1¼ parts of charcoal powder, the mixture is moistened and placed in an iron crucible, and calcined at red heat for 6 to 10 hours; the cooled mass broken into small lumps is again moistened with water and then exposed to the action of sulphurous acid; the resulting product is dissolved in water, filtered, concentrated by evaporation, and left to crystallise. According to E. Kopp's method, carried out industrially by Max Schaffner at Aussig, hyposulphite of lime is first prepared by causing sulphurous acid to act upon sulphuret of calcium (soda waste). The lixiviated mass is treated with sulphate of soda, the result being the formation of soluble hyposulphite of soda and practically insoluble sulphate of lime. Very recently the pentathionic acid (S_5O_5,H_2O), obtained in large quantity as a by-product of the reaction between sulphuretted hydrogen and sulphurous acid in preparing sulphur, has been converted into hyposulphite of soda by boiling with soda lye ($2S_5O_5,H_2O + 3H_2O = 5S_2O_2,H_2O$).

As hyposulphite of soda possesses the property of readily forming with oxide of silver a soluble double salt, hence dissolving easily such insoluble compounds as chloride and iodide of silver, it is employed in photography and in the hydrometallurgical extraction of silver. Being a solvent for iodine it is used in chemistry for purposes of volumetrical analyses. A mixed solution of sulphite and hyposulphite of soda dissolves malachite and blue copper ore, forming hyposulphite of protoxide of copper and sodium. Stromeyer has applied this reaction to the hydrometallurgical extraction of copper. Hyposulphite of soda is also used for preparing antimonial cinnabar and aniline green; the hyposulphites of lead and copper have been proposed as a paste for lucifer matches. The property possessed by hyposulphite of soda of fusing at a comparatively low temperature in its water of crystallisation, and of readily solidifying on cooling, has been utilised by Fleck, in the sealing of glass tubes containing explosive compounds to be used under water in torpedoes. The enormous consumption of hyposulphite of soda may be readily inferred from the fact that the chemical factory near Aix-la-Chapelle produces 2000 cwts., and the factory at Aussig, Austria, 6000 cwts. of this salt annually.

Manufacture of Sulphuric Acid.

Sulphuric acid, H_2SO_4, consists in 100 parts of 81 parts of anhydrous sulphuric acid and 18·5 parts of water.

Sulphuric Acid. There are in the trade two distinct varieties of this acid:—

a. Fuming, or Nordhausen sulphuric acid (oil of vitriol), obtained by distillation from sulphate of iron, bisulphate of soda, sulphate of peroxide of iron, or by the decomposition of sulphate of soda by means of boric acid in the preparation of borax.

b. Ordinary sulphuric acid, known abroad as English sulphuric acid, prepared by the oxidation of sulphurous acid by means of nitrous acid, or, very rarely, separated from native sulphates.

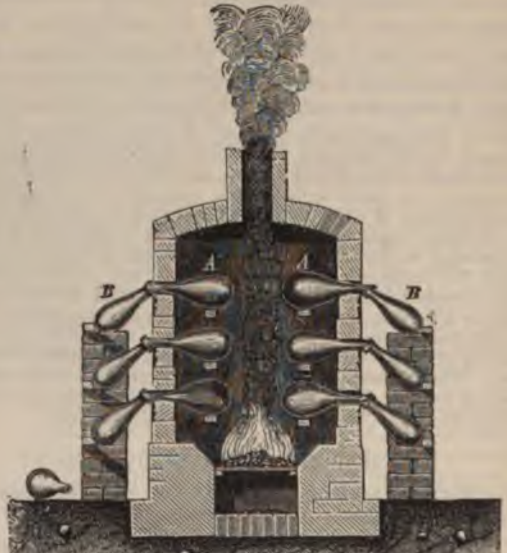
Fuming Sulphuric Acid. At a red heat all sulphates, except those of the alkalies and alkaline earths, are decomposed, and therefore may be employed in the preparation of fuming sulphuric acid; but on account of its cheapness sulphate of iron is preferred. This salt, on exposure to red heat, is decomposed into anhydrous sulphuric acid and sulphurous acid:—

$$\text{Sulphate of iron, } 2FeSO_4\text{, yields} \left\{ \begin{array}{l} \text{Peroxide of iron, } Fe_2O_3, \\ \text{Sulphuric acid, } SO_3, \\ \text{Sulphurous acid, } SO_2. \end{array} \right.$$

Anhydrous sulphuric acid would indeed be obtained from sulphate of iron if it were possible to procure the salt perfectly anhydrous, but as this cannot be done without decomposition, some water is always retained, the result being the compound known as fuming sulphuric acid, that is to say, a mixture of anhydrous and ordinary acid (H_2SO_4), the former in very variable quantities.

Fuming sulphuric acid is prepared on the large scale in the following manner:—The solution of sulphate of iron is first evaporated to dryness, and dried in open vessels as much as possible. The dry saline mass, vitriol-stone it is termed in Germany, is next transferred to fire-clay flasks, A, Fig. 92, placed in a galley-furnace, the necks passing through the wall of the furnace, and being properly secured to the necks of the receivers, B B. Into each of the flasks 2·5 lbs. of vitriol-stone are put: on the first application of heat only sulphurous acid and weak hydrated sulphuric acid come over, and are usually allowed to escape, the receivers not being securely luted until white vapours of anhydrous sulphuric acid are seen. Into each of the receiving flasks 30 grms. of water are poured, and the distillation continued for 24 to 36 hours. The retort flasks are then again filled with

FIG. 92.



raw material, and the operation repeated four times before the oil of vitriol is deemed sufficiently strong. The residue in the retorts is red oxide (peroxide) of iron, still retaining some sulphuric acid. The quantity of fuming acid obtained amounts to 45 to 50 per cent. of the weight of the dehydrated sulphate of iron employed; at Davidsthal, in Bohemia, 14 cwts. of vitriol-stone yield in thirty-six hours, 5½ cwts. of fuming sulphuric acid.

It is preferable, however, to use sulphate of peroxide of iron instead of the dried protosulphate; the sulphate of the peroxide can be readily prepared by means of the peroxide and ordinary sulphuric acid. Frequently the fuming acid is prepared by passing anhydrous sulphuric acid, obtained by calcining perfectly dehydrated protosulphate of iron, or, better still, the persulphate of iron, into ordinary oil of vitriol. Fuming sulphuric acid is now and then prepared from the bisulphate of soda left after the preparation of nitric acid from Chili-saltpetre. In France calcined sulphate of soda and boracic acid are intimately mixed and calcined, and the vapours of anhydrous sulphuric acid disengaged are absorbed by strong ordinary sulphuric acid. Fuming sulphuric acid is an oily liquid of a brown yellow or deep brown colour; it emits the pungent smell of sulphurous acid, fumes on being exposed to air, and yields on being heated vapours of anhydric sulphuric acid: the sp. gr. varies from 1·86 to 1·92. It is industrially hardly used for any other purpose than dissolving indigo, 1 part of the latter requiring for its solution 4 parts of fuming and 8 parts of ordinary sulphuric acid.

Ordinary or English Sulphuric Acid. The concentrated sulphuric acid (H_2SO_4), oil of vitriol of commerce, consists in 100 parts of 81·5 parts of anhydrous acid and 18·5 of water. The preparation of this acid on the large scale in leaden chambers dates from the year 1746, when Dr. Roebuck, of Birmingham, erected the first leaden chamber at Prestonpans, near Edinburgh.

The *rationale* of the manufacture of sulphuric acid by the chamber process, in which sulphurous acid, nitric or nitrous acid, and water are employed, is, according to the latest researches of R. Weber (1866) and Winkler (1867), the following:—The oxidation of the sulphurous acid to sulphuric acid takes place in the leaden chambers under the influence of the vapour of water at the expense of the oxygen of the nitrous acid, which is converted into deutoxide of nitrogen. It is necessary, however, that the nitrous acid be first absorbed in plenty of water, which takes up the free nitrous acid, and decomposes the hyponitric acid, a process greatly promoted by the presence in the chamber of sulphurous acid purposely introduced. The water, usually in the form of steam, because practical experience proves that a certain elevation of temperature is required, acts in this process as in others wherein sulphurous acid effects reduction. By the presence of atmospheric air in the chamber the deutoxide of nitrogen is oxidised into hyponitric or nitrous acid, and this acid again decomposed by sulphurous acid; if the conditions are favourable the process is continuous. It occasionally happens that the nitrous acid in contact with sulphurous acid and excess of water forms protoxide of nitrogen, of course causing a loss of the efficient oxides of the nitrogen. The formation of the so-called chamber crystals, consisting according to R. Weber of ($H_2SO_4 + N_2O_3,SO_3$) only takes place when the process is not well managed, and is chiefly due to want of water.

Present Manufacture of Sulphuric Acid. Although the use of leaden chambers is due to an Englishman, the present mode of manufacturing sulphuric acid was invented (1774) by a calico printer at Rouen, and improved by the celebrated Chaptal. The apparatus consists essentially of four parts, viz.—1. A furnace, F, Fig. 93, where, by the combustion of sulphur or pyrites, sulphurous acid is formed; the sulphurous acid, carrying with it the nitrous vapours prepared in the sulphur burner by means of a peculiar contrivance, escapes from the furnace through the tube, T.* 2. An apparatus filled with coke through which mixed sulphuric and nitric acids percolate. 3. A number of leaden chambers, A, A′, and A″, wherein, under the influence of high pressure steam, the sulphuric acid is formed. 4. A large apparatus, K, known as

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* In order to convert 1 kilo. of sulphur into sulphuric acid, the following quantities of air are required:—

When the sulphur is present in free state, 5275 litres of air, containing 4220 litres of nitrogen.

When the sulphur is present as pyrites, 6595 litres of air, containing 5276 litres of nitrogen.

Gay-Lussac's condenser, filled with coke, through which sulphuric acid of 66° B. (= 1·84 sp. gr.) percolates, the aim being to take up the nitric and hyponitric acids, not the deutoxide of nitrogen as was believed before Winkler elucidated this point, from the gases which flow into the last chamber previously to being discharged. The furnace or burner, as it is technically called (see Fig. 94), is built of bricks; at a height of 80 centims. from the floor a stout cast-iron plate is placed so as to have a slight inclination towards the front. The walls are also covered with heavy cast-iron plates. In front of the burner are three or six large openings, P, P′, P″, which can be closed by iron doors fitted with wooden handles. On the bed or bottom plate three iron rails or ledges, each 10 centims. high, are placed to divide the bottom of the furnace into three or six compartments. At H, H′, and H″ are the holes for the necessary supply of air. On the top plate is firmly fixed the tube, T, which conveys the gases generated in the burner to the leaden chamber of each section or compartment. The burner is charged with about 50 kilos. of sulphur; this is kindled at the top, the draught of air through H, H′, and H″ being so regulated as to cause

FIG. 93.

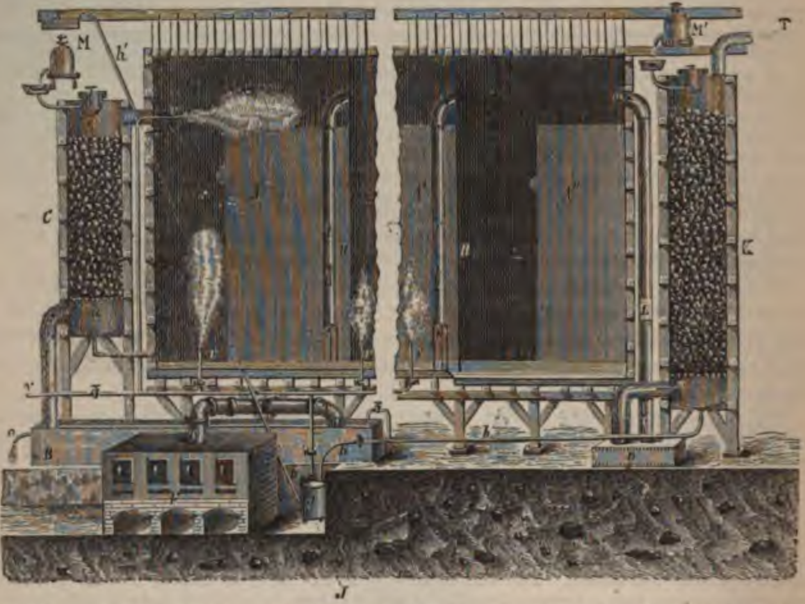
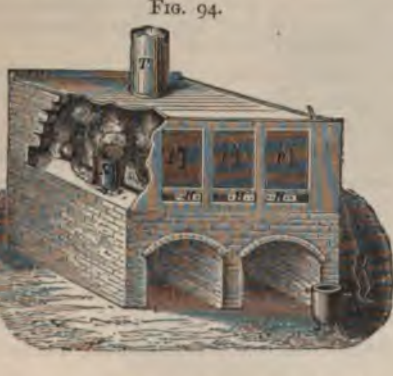


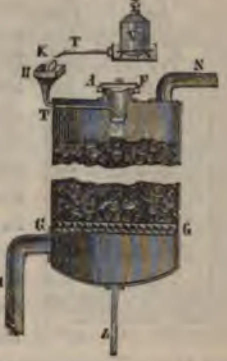
FIG. 94.



the sulphur to be burnt off without becoming sublimed, for if any sulphur were volatilised it would cause the sulphuric acid to be turbid and milky.[*] Not only does the burner supply sulphurous acid, but also the nitric acid or nitrous vapours required in the leaden chamber; these are generated from a mixture of nitrate of soda and sulphuric acid at 52° B. (= 1·56 sp. gr.) placed in the cast-iron pot, N, which when filled is placed on the burning sulphur.

The construction and arrangement of the *denitrificateur* is shown in Fig. 95. At G is placed an iron grating covered with thick perforated sheet lead; the vapours and gases generated in the burner pass through M into the space immediately below G, upon which a column of coke is placed, and kept saturated with sulphuric acid strongly charged with nitric acid, obtained by the condensation of the gases from the last chamber. This acid is forced by means of compressed air from the vessel Y into the Mariotte bottle, V, and passes thence through T into H, thence by T′ to the coke, over which it is delivered in fine jets by means of a perforated plate fitted to the lower part of the cover A. The acid coming in contact with the warm gases from the chamber yields to them, in the state of vapour, all the nitrous compounds dissolved in the sulphuric acid, and charged with these vapours the gases pass through *m*, Fig. 93, into the leaden chambers. The denitrified sulphuric acid runs off through the tube *t* into a reservoir.

FIG. 95.



The formation of sulphuric acid takes place in the leaden chambers or chamber. In many cases, especially abroad, only one large chamber is worked, which is then, as shown in Fig. 93, divided by the leaden plates R R′, technically termed curtains, into three or more compartments, these curtains reaching to the bottom into the acid collected there. If several chambers are worked, communication is maintained by means of leaden tubes. The tubes *v v′ v″*, convey steam to the chambers. The chambers are not usually all of the same size, one being considerably larger than the others; in the largest most of the acid is generated. The gases and vapours contained in the last chamber being almost free from sulphurous acid, and consisting mainly of atmospheric air and nitrous vapours, are conveyed through T′ to the leaden reservoir, D, where the last traces of sulphuric acid are deposited. The action of Gay-Lussac's condenser, K, is based upon the fact that concentrated sulphuric acid absorbs and combines with nitrous acid. The apparatus consists essentially of a column of coke 8 to 10 metres in height, through which strong sulphuric acid, 62° or 64° B., percolates, the flow being regulated by the apparatus shown in Fig. 95. The acid saturated with nitrous acid is conveyed by the tubes *h h* into a reservoir, O, from which it is again forced by means of the monte-acid to the Mariotte flask, M. By the tube T‴, the gases are conveyed to the chimney stalk of the works. As regards the cubic capacity of the leaden chambers, each 20 kilos. of sulphur consumed in twenty-fours hours requires 30 cubic metres (about 100 cubic feet) capacity; as this quantity of sulphur corresponds to 60 kilos. of hydrated sulphuric acid, a chamber of the capacity mentioned yields 2·5 kilos. of sulphuric acid per hour. One hundred parts of sulphur require from 6 to 8 parts of nitrate of soda, but if pyrites is employed this quantity is often increased. Also when pyrites is burnt larger chambers are used. Lately Gay-Lussac's condenser has, in many cases, fallen into disuse, on account of the low price of Chili-saltpetre, and the expense of keeping the apparatus in working order.

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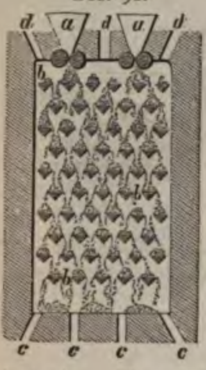
[*] According to theory, 1 molecule of sulphur requires only 3 molecules of oxygen, viz., 2 to form sulphurous acid, and 1 to convert the latter into sulphuric acid; that is to say, 1 kilo. of sulphur requires 1500 grms. = 1055 litres of oxygen = 5275 litres of air, in which 4220 litres of nitrogen are contained. In order to regulate this supply of air many contrivances have been adopted, among them the anemometer invented by Combes; this is fitted to the sulphur burner by means of a tube, through which the air supplied has to pass. In England reliance is placed upon the skill of the workmen who regulate the draught, as it is termed, simply by the slides in the doors of the burners.

The air discharged from the chambers should not contain more than 2 to 3 per cent. of oxygen. By careful management and with good apparatus the maker may succeed in obtaining from 100 kilos. of sulphur 306 kilos. of strong acid at 1·84 sp. gr.; but the usual quantity from 100 kilos. of sulphur is seldom more than 280 to 290 kilos.

Use of Pyrites for the Preparation of Sulphurous Acid. Instead of sulphur native minerals containing that element are frequently employed for the preparation of sulphurous acid. Among these minerals, iron pyrites, bisulphuret of iron, FeS_2, containing 53·5 per cent. of sulphur, is the most largely used. The pyrites are calcined in peculiarly constructed kilns, built with fire-bars, the spaces between which may be adjusted by means of a key, and the admission of the air required for combustion regulated with great nicety. The best pyrites oven known on the Continent is Gerstenhöfer's, invented in 1864; the principle of this oven, Fig. 96, is that the pyrites is made to fall through and meet the column of heated air supporting the combustion. In order to prolong the fall of the powdered pyrites, terraces or banks are built at intervals in the shafts. The broken up pyrites falls through the funnels *a*, provided with grooved rollers to pulverise it, on to the banks *c*, from one terrace, as they are termed, to another. As the furnace has been previously made red-hot, the sulphur ore ignites and burns off, aided by a moderate blast at *c*. The sulphurous acid formed is discharged by the channels *d* into the sulphuric acid chambers, sometimes being first conveyed to an ante-room, where the dust of the pyrites mechanically mixed with the gases is deposited.

Fig. 96.



The nitrous acid vapours are generated in a manner similar to that used for sulphur. It will be seen that when pyrites is burnt, a far larger quantity of air is required for the same quantity by weight of sulphur, amounting for 1 kilo. of pyrites to 6595 litres of air. This excess is due to the oxidation of the iron of the pyrites, and the large bulk of nitrogen accompanying the excess of oxygen

$$(2FeS_2 + 11\,O = 4SO_2 + Fe_2O_3).$$

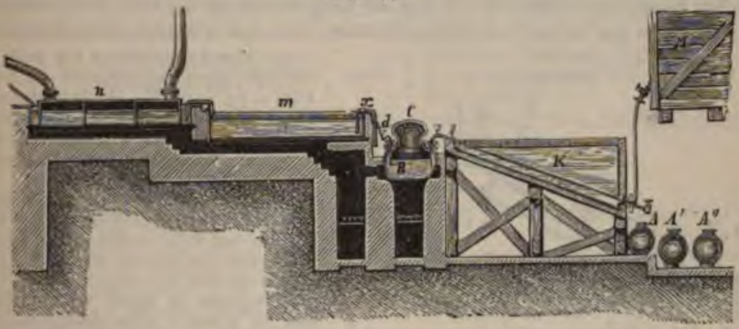
According to Fortman, the gases from the pyrites burners also contain vapours of anhydrous sulphuric acid. Among the substances found in the flue dust of the pyrites burners are selenium and thallium. Carstanjen found thallium to the amount of 3·5 per cent. in the flue dust of a sulphuric acid works near Berlin, where a pyrites from Mezzen was used.

Chamber Acid. As soon as the acid formed in the leaden chambers has acquired a sp. gr. of 1·5 = 50° B. = 104° Twaddle, it is run off into a reservoir, and is frequently used in that state of concentration for the purpose of preparing artificial manures or superphosphates in alkali works, for the preparation of nitric acid, and for other purposes. This acid may be freed from arsenic by treating with sulphuretted hydrogen.

Concentration of Sulphuric Acid. This operation is effected in two different stages, the first being carried on in leaden pans, the latter in platinum or glass retorts. Weak and cold sulphuric acid does not act powerfully on lead, but as soon as the acid becomes concentrated, and especially when hot, the lead is dissolved, sulphurous acid given off, and sulphate of lead formed. Many sulphuric acid makers concentrate their acid to 60° B. = 1·71 sp. gr., in leaden pans; others, however, concentrate in leaden pans to 55° B. = 1·59 sp. gr. only.

Concentration in Leaden Pans. The pans employed for this purpose are rectangular in shape, rather shallow, but long and wide, and supported by iron plates, so that the fire shall not strike the bottom directly. The modes of placing and construction are shown in Fig. 97; the acid is more strongly heated in the pan, *m*, while in *n* it is only affected by the hot air. The depth of the acid in the pans varies from 24 to 36 centims. As soon as the acid is of about 1·71 sp. gr., it is further deprived of its excess of water, in glass, porcelain, or platinum vessels.

FIG. 97.



Platinum Retorts. Platinum retorts are now very frequently employed, although it is clear that these vessels, considering the high price of platinum, are expensive, the price depending upon the weight, size, and workmanship. Messrs. Johnson, Matthey, and Co, Hatton Garden, London, are among the best makers of these and other platinum apparatus.

FIG. 98.

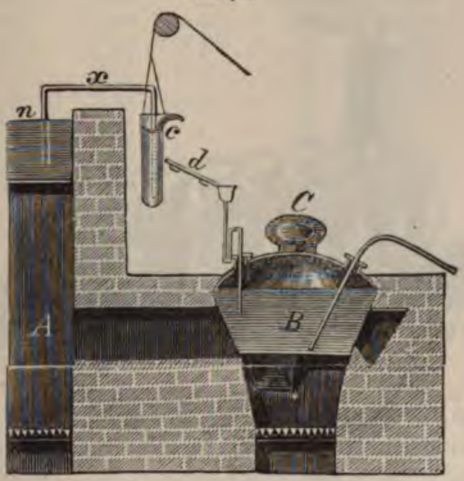
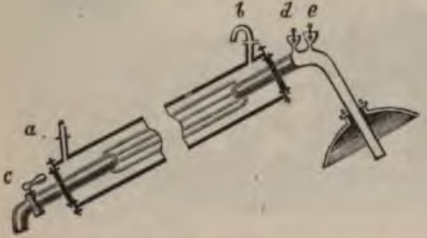


Fig. 98 is an enlarged view of the platinum retort, represented together with the leaden pans in Fig. 97. The hearth communicates with A. By means of the syphon, *x*, the acid from *n* can be transferred to B; the longer leg of *x* dipping into a leaden vessel, which admits of being lowered to *d* by the aid of the pulley. The acid then runs from the spout *c* into the channel *d*, and thence, through the funnel-tube, into the retort, B. The head, C, communicates by means of tubing, not shown in the cut, with a worm, where the water and very weak acid mechanically carried over with the steam are condensed. When the temperature of the acid in the platinum still attains to 310° to 320°, strong acid comes over, and is condensed in the worm.

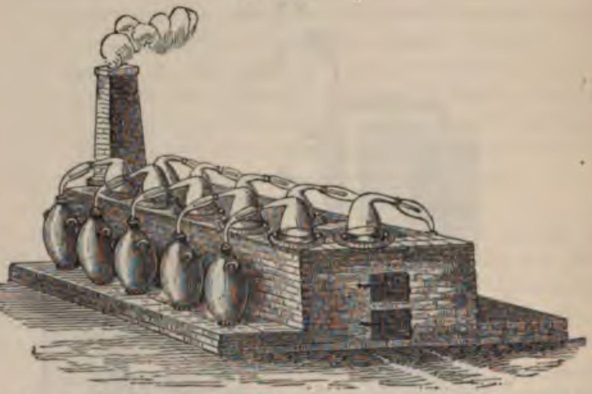
FIG. 99.



In order to withdraw the acid from the still, when concentrated to 1·78 to 1·80(=63° to 66° B.), the Breant syphon, Fig. 99, is used. It is made of platinum; the outer leg has a length of about 5 metres, and is surrounded by a copper tube 15 centims. wide by 36 centims. long, which can be filled at *a* from the tank M (see Fig. 97) with cold water, the outlet for the hot water being at *b*. In order to increase the surface the main syphon tube is divided into four narrower tubes. The syphon is filled with sulphuric acid by *d* and *e* after closing the tap *c*. The very hot acid cools while flowing through the platinum tubes, and is collected in jars, A, A′, A″,

Concentration in Glass Retorts. When glass retorts of good quality and sufficiently large size can be obtained at a cheap rate, they are very frequently employed, being placed to the number of ten or more (Fig. 100) in sand-baths. The retorts are connected to earthenware balloons, in which the acid fumes are condensed. 70 per cent. of the strong sulphuric acid sold in this country is concentrated in glass retorts. Very recently cast-iron vessels have been used for concentrating sulphuric acid.

FIG. 100.



Other Methods of Sulphuric Acid Manufacture. Many methods of preparing sulphuric acid have been suggested, but hitherto none have anywhere superseded the process generally adopted. For this reason it is necessary to mention a few only of the reactions upon which these methods are based. Hahner oxidises sulphurous acid with chlorine, care being taken that steam is present at the time:—

$$\left.\begin{array}{l}\text{Sulphurous acid, } SO_2\\ \text{Aqueous vapour, } 2H_2O\\ \text{Chlorine, } 2Cl\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Sulphuric acid, } H_2SO_4,\\ \text{Hydrochloric acid, } 2ClH.\end{array}\right.$$

Persoz's method is based upon the following reactions:—1. Oxidation of sulphurous acid by means of nitric acid, the latter being heated to 100° and diluted with four to six times its bulk of water. 2. The vapours of hyponitric acid are again converted to nitric acid by the oxygen of the air and steam. In this process the leaden chambers are replaced by a series of large stone-ware Woulfe's bottles. Although enormous quantities of gypsum are found native, all attempts to prepare sulphuric acid from this mineral on an industrial scale have failed. Gypsum is decomposed, by superheated steam and at red heat, into sulphuric acid, oxygen, and sulphurous acid, leaving caustic lime in the retort. Shanks mixes gypsum with chloride of lead and water at about 60°.

$$\left.\begin{array}{l}\text{Gypsum, } CaSO_4+2H_2O\\ \text{Chloride of lead, } PbCl_2\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Chloride of calcium, } CaCl_2,\\ \text{Sulphate of lead, } PbSO_4,\\ \text{Water, } 2H_2O.\end{array}\right.$$

The chloride of calcium solution having been withdrawn from the precipitate of sulphate of lead, the latter is heated with hydrochloric acid:—

$$\left.\begin{array}{l}\text{Sulphate of lead, } PbSO_4\\ \text{Hydrochloric acid, } 2ClH\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Chloride of lead, } PbCl_2,\\ \text{Sulphuric acid, } H_2SO_4.\end{array}\right.$$

Properties of Sulphuric Acid. The most highly concentrated sulphuric acid contains 18·46 per cent. of water; its formula is H_2SO_4; sp. gr. = 1·848. In a perfectly pure state it is a colourless liquid, but commonly is more or less yellow or brown, owing to the presence of organic matter. It destroys many organic substances, leaving a carbonaceous residue. This sulphuric acid does not fume on exposure to air; it is very hygroscopic, and when left exposed to air, gradually absorbs fifteen times its bulk of water. When mixed with water great heat is evolved. The boiling-point of the most highly concentrated acid is 338°.

The following table gives the quantity of anhydrous sulphuric acid contained in sulphuric acid at 15·5° C.:—

Hydrated Sulphuric acid.	Sp. gr.	Anhydrous acid.	Hydrated Sulphuric acid.	Sp. gr.	Anhydrous acid.
100	1·8485	81·54	76	1·6630	61·97
99	1·8475	80·72	75	1·6520	61·15
98	1·8460	79·90	74	1·6415	60·34
97	1·8439	79·09	73	1·6321	59·55
96	1·8410	78·28	72	1·6204	58·71
95	1·8376	77·40	71	1·6090	57·89
94	1·8336	76·65	70	1·5975	57·08
93	1·8290	75·83	69	1·5868	57·26
92	1·8233	75·02	68	1·5760	55·45
91	1·8179	74·20	67	1·5648	54·63
90	1·8115	73·39	66	1·5503	53·82
89	1·8043	72·57	65	1·5390	53·00
88	1·7962	71·75	64	1·5280	52·18
87	1·7870	70·94	63	1·5170	51·37
86	1·7774	70·12	62	1·5066	50·55
85	1·7673	69·31	61	1·4960	49·74
84	1·7570	68·49	60	1·4860	48·92
83	1·7465	67·68	59	1·4760	48·11
82	1·7360	66·86	58	1·4660	47·29
81	1·7245	66·05	57	1·4560	46·58
80	1·7120	65·23	56	1·4460	45·68
79	1·6993	64·42	55	1·4360	44·85
78	1·6870	63·60	54	1·4265	45·03
77	1·6750	62·78	53	1·4170	43·22

Comparative degrees of Baumé and Twaddle, with the corresponding sp. gr.:—

Degrees Baumé.	Degrees Twaddle.	Sp. gr.
66	168	1·84
63	154	1·77
60	140	1·70
57	130	1·65
50	104	1·52
45	88	1·44
40	76	1·38
35	62	1·31
30	52	1·26
25	42	1·21

The reader desirous of more information as to the specific gravities indicated by Baumé's hydrometers is referred to the "Chemical News," vol. xxiv., p. 28, *et seq.*

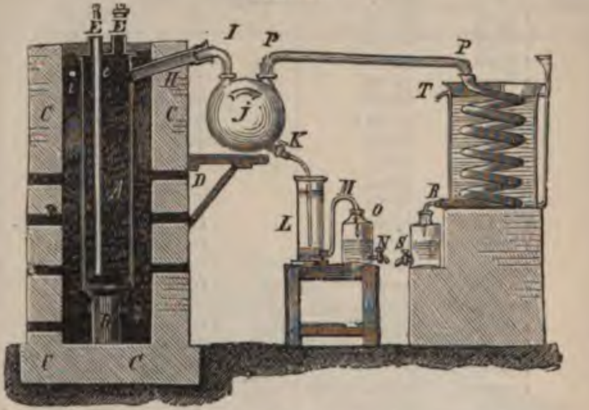
The uses of sulphuric acid are so numerous that it would be impossible to mention all of them, sulphuric acid being to chemical industry what iron is to the mechanical. Sulphuric acid is employed in preparing a great many other acids, among them nitric, hydrochloric, sulphurous, carbonic, tartaric, citric, phosphoric, stearic, oleic, and palmitic. Further, sulphuric acid is used in making superphosphates, soda, sulphate of ammonia, alum, sulphates of copper and iron, in paraffin and petroleum refining, silver refining, manufacture of garancine, garanceux, and other madder preparations, manufacture of glucose from starch, to dissolve indigo, &c.

SULPHIDE OF CARBON.

Sulphide of Carbon. This compound, consisting in 100 parts of 15·8 parts of carbon and 84·2 of sulphur, formula CS_2, was discovered in 1796 by Lampadius, at Freiburg. It is obtained by causing the vapour of sulphur to pass over red-hot coals, or by distilling an intimate mixture of native metallic sulphurets with charcoal or coke. The largest quantity of sulphide of carbon is obtained, according to Sidot and W. Stein, at not too high a red heat, that is to say, at what is termed in gas-works orange-red heat.

Sulphide of carbon is best manufactured by means of Peroucel's apparatus (Fig. 101). A is a fire-clay gas-retort, supported on the fire-clay block B; E and E are openings, one being that of a porcelain tube firmly cemented into the cover of A, serving for the introduction of sulphur; the other opening is for the introduction of pieces of coke, with which, before the operation commences, the retort is filled. The vapours of the sulphide of carbon pass through the tubes H and I into the vessel J, wherein part of the sulphide is condensed and flows through K into the flask, L, filled with water, thence through M into O, finally being run off by the tap, N. Any vapours not condensed in J pass through P P into the worm, T, the condensed sulphide being collected in S. The crude sulphide of carbon is rectified by re-distillation over zinc or over bichloride of mercury by means of steam or a water-bath. If the bichloride is employed, the crude sulphide should remain in contact with the salt for at least twenty-four hours before re-distillation. With the apparatus described, the retort being 2·1 metres in height and 0·3 metre in diameter, 2 cwts. of crude sulphide

FIG. 101.



of carbon may be prepared in twelve hours. The quantity of sulphide resulting from a given weight of materials is always much less than the quantity theoretically obtainable; this is, of course, partly due to an unavoidable loss of liquid, and probably to the formation of monosulphide of carbon (CS), a compound corresponding to carbonic oxide. Crude sulphide of carbon contains usually 10 to 12 per cent. of sulphur in solution, and also sulphuretted hydrogen. To purify the crude sulphide, bleaching-powder solution is added to the liquid in the retort, into which steam at 15 lbs. pressure is forced to effect the reaction between the chloride of lime and the impurities present in the sulphide of carbon. Sulphide of carbon is usually kept under water. When pure, sulphide of carbon is a colourless liquid, strongly refractive, exhibiting extremely bright colours when in the sunlight. Its odour somewhat resembles that of chloroform; the taste is aromatic. Its sp. gr. = 1·2684; the boiling-point is 46·5°, consequently the liquid is very volatile at the ordinary temperature of the air.

Carbon. Sulphide of carbon does not combine with water or spirits of wine. It is not soluble in every proportion in water (see "Chemical News," vol. xxiv., p. 34); in ether and chloroform, however, it is freely soluble. Sulphide of carbon is an excellent solvent for resins, essential and fixed oils, caoutchouc, gutta-percha, camphor, sulphur, phosphorus, and iodine. It is highly inflammable, burning with a red-blue flame; the products of complete combustion are sulphurous and carbonic acids. The vapour of sulphide of carbon with oxygen or air constitutes an explosive mixture; the light given by a mixture of deutoxide of nitrogen and sulphide of carbon is very intense, and has been employed in photography. To Mr. Fisher, of Birmingham, is due the honour of having first prepared sulphide of carbon for industrial purposes. At the present day these purposes are very varied, but consist chiefly of the vulcanisation of caoutchouc, the extraction of fat from bones, and oils from oil seeds and olives, the extraction of sulphur from its concomitant rocks, and of fat from crude wool. Sulphide of carbon is also used in electro-plating to obtain by its addition to the silver-bath a bright and polished surface. It is highly valued for killing vermin in corn.

Chloride of Sulphur. Chloride of sulphur (Cl_2S_2), important only in its technical use for the vulcanising of caoutchouc, is an oily fluid, sp. gr. 1·60, of a brown colour, fuming on exposure to air. It boils at 144°. On being mixed with water it is decomposed, yielding sulphurous and hydrochloric acids, a very small quantity of sulphuric acid, and sulphur. Chloride of sulphur converts rape-seed oil into a mass resembling caoutchouc, and linseed oil into a varnish. Chloride of sulphur is prepared by passing chlorine gas over sulphur heated to 125° to 130°; the product is rectified by distillation.

HYDROCHLORIC ACID AND GLAUBER'S SALT, OR SULPHATE OF SODA.

Hydrochloric Acid. The commercial article known as hydrochloric or muriatic acid, or spirits of salt, is, as has been explained in the manufacture of soda, a solution of the gas given off during the decomposition of common salt by sulphuric acid. In order to effect this condensation, the gas is conveyed to the coke columns, or in many instances is prepared and condensed by the aid of the apparatus shown in section in Figs. 102 and 103, and in plan in Fig. 104. The apparatus consists of several cast-iron cylinders, 1·7 metres long by 0·7 metre diameter, closed similarly to gas retorts by lids luted with clay. One of the lids is provided with an opening, *o*, into which is fitted the stoneware or leaden pipe, *a*, conveying the hydrochloric acid to the condensing apparatus. The other, or posterior lid, is also provided with an opening, *d*, through which is passed the tube of a leaden funnel, so that after the retort is filled with salt, sulphuric acid may be poured in. The construction of the furnace, in which two retorts are usually placed, allows the flame of the fire at O to play round the cylinders before reaching the flue leading to the chimney, F. B is an arch covering the furnace. The first stage of the operation is to fill each cylinder with 150 kilos. of salt or chloride of potassium, in localities where the latter is abundant. The lids or covers are next luted on, and the fire kindled. The required quantity of strong sulphuric acid is now poured into the retort, and the funnel having been withdrawn from *d*, the hole is closed by a clay plug. As soon as the reaction is over, the 180 kilos. of sulphate of soda produced are removed, and the operation repeated. The condensation apparatus, Figs. 102 and 104, consists of

FIG. 102.

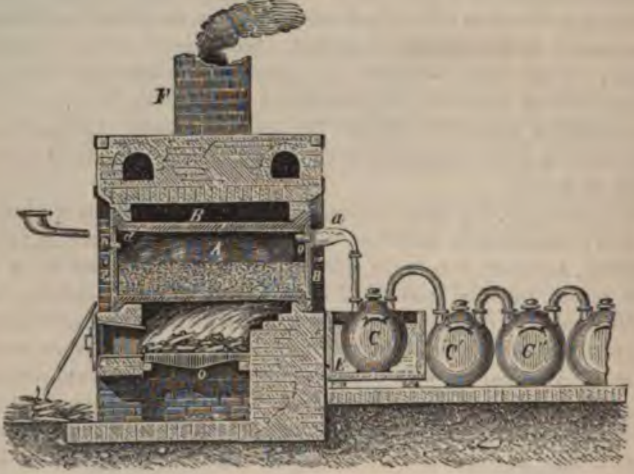
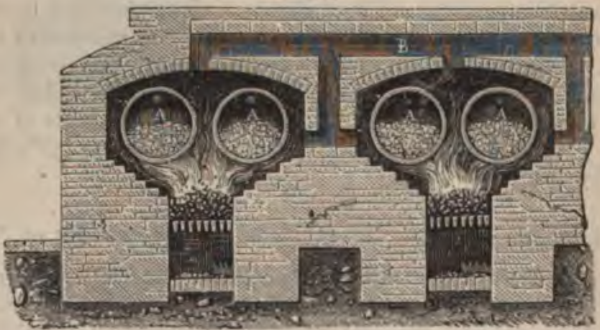
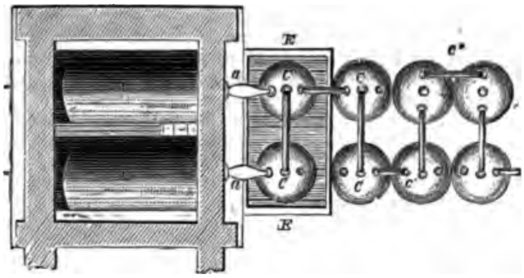


FIG. 103.



rows of Woulfe's bottles partly filled with water, care being taken to place the first pair of these bottles in a tank of cold water. The condensation of the last portions of the hydrochloric acid gas is effected either by the aid of coke columns, or in leaden chambers, into which fine jets of cold water are injected on all sides.

FIG. 104.



Properties of Hydrochloric Acid. Crude commercial hydrochloric acid is commonly a yellow liquid, this colour being due to chloride of iron. It has a caustic sour taste, and fumes on exposure to air. At 20° water is capable of absorbing 475 times its own bulk of hydrochloric acid gas; a saturated solution contains 42·85 per cent. of gas, the sp. gr. being = 1·21. The following table shows the sp. gr. of hydrochloric acid at various degrees of concentration, and the quantity of pure acid (real gas) contained at 70°:—

Specific gravity.	Degrees Baumé.	Degrees Twaddle.	Percentage of acid.	Specific gravity.	Degrees Baumé.	Degrees Twaddle.	Percentage of acid.
1·21	26	42	42·85	1·10	14·5	20	20·20
1·20	25	40	40·80	1·09	12	18	18·18
1·19	24	38	38·88	1·08	11	16	16·16
1·18	23	36	36·36	1·07	10	14	14·14
1·17	22	34	34·34	1·06	9	12	12·12
1·16	21	32	32·32	1·05	8	10	10·10
1·15	20	30	30·30	1·04	6	8	8·08
1·14	19	28	28·28	1·03	5	6	6·06
1·13	18	26	26·26	1·02	3	4	4·04
1·12	17	24	24·24	1·01	2	2	2·02
1·11	15·5	22	22·22				

Uses of Hydrochloric Acid. Hydrochloric acid is very largely employed in the manufacture of chlorine, sal-ammoniac, chloride of antimony, glue, phosphorus, in the preparation of carbonic acid for the manufacture of artificial mineral waters, in beet-root sugar works, bleach works, hydro-metallurgy, and alone or mixed with nitric acid for dissolving various metals.

Glauber's Salt. Sulphate of soda, or Glauber's salt, consists in 100 parts of 19·3 soda, 24·7 sulphuric acid, and 56 water; formula, $Na_2SO_4 + 10H_2O$; anhydrous, Na_2SO_4, in 100 parts—soda, 43·6; sulphuric acid, 56·4. It is prepared as described under hydrochloric acid by decomposing common salt with sulphuric acid. It is also found native as Thenardite (Na_2SO_4), Brogniartine or Glauberite ($Na_2SO_4 + CaSO_4$), and it occurs in sea-water and some mineral waters, as in those of Püllna and Carlsbad.

Sulphate of soda is indirectly obtained by various processes, among which are—1. The double decomposition of common salt and sulphate of magnesia or kieserite from the mother-liquor of sea-water, or of salines when exposed to a low temperature either naturally in water or artificially by the assistance of Carré's ice-making machine. 2. Longmaid's process of roasting sulphuret of iron or copper with common salt. 3. Calcination of kieserite or magnesian sulphate with common salt. 4. Kuhlmann's process, the calcination of sulphate of magnesia and nitrate of soda, hyponitric acid and sulphate of soda being formed. 5. As a by-product of paraffin and petroleum refining. The sulphate of soda of the alkali works contains on an average 93 to 97 per cent. of the pure salt, the remainder being chiefly chloride of sodium.

Uses of Sulphate of Soda. This salt is extensively employed in the manufactures of soda, ultramarine, and glass. In the last case the sulphate is mixed with coal and silica, and calcined, its sulphuric acid being reduced to sulphurous acid, which is volatilised, while a silicate of soda is formed. Sulphate of soda when thus employed should be purified from all traces of iron by being dissolved in water, some lime added to the solution, and the clear liquid evaporated to dryness. Sulphate of soda is used in metallurgy in the treatment of some kinds of antimonial ores, the sulphuret of antimony found near Bouc and Septèmes, France, &c. It is also employed in certain processes of wool-dyeing.

Bisulphate of Soda. This salt ($NaHSO_4$) is obtained in large crystals when 1 molecule of sulphate of soda and 1 molecule of sulphuric acid are dissolved in water and the solution left to evaporate slowly. One of the chief uses of the bisulphate is in a mixture with abraum salt containing chloride of magnesium, employed for removing zinc from lead. As a by-product sulphate of soda is obtained in the manufacture of nitric acid from nitrate of soda and sulphuric acid, and by heating cryolite with sulphuric acid.

BLEACHING-POWDER AND HYPOCHLORITES.

Chlorine. It is one of the most valuable properties of chlorine that it destroys organic pigments and miasmata, and is hence useful as a bleaching agent, and as a disinfectant. It is also employed as an oxidising agent in the extraction of gold from pyritical ores.

At the ordinary temperature and pressure of the atmosphere chlorine is a greenish-yellow gas, its sp. gr. = 1·33; it possesses a peculiarly disagreeable, irritating odour, and is very soluble in water, 1 volume absorbing 2·5 volumes of gas, forming the well-known *aqua chlorii*, or *acidum muriaticum oxygenatum aqua solutum* of the pharmaceutists, and the chlorine water of the scientific chemist. The bleaching property of chlorine gas, possessed also by its solution, is due to the great affinity of chlorine for hydrogen, so that the chlorine while seizing upon the hydrogen of the organic body in most instances causes the simultaneous decomposition of water, and by the formation of ozone destroys the organic colouring matter, hydrochloric acid being at the same time formed, a fact requiring attention in the use of chlorine as a bleaching agent. When linen, or rather flax, raw cotton, and paper pulp are bleached by chlorine, the fibre, really cellulose, is not acted upon, but only the colouring matter is oxidised by the ozone formed. Chlorine cannot be used to bleach animal matters, or such as contain nitrogen, these becoming yellow by its action. Chlorine is not suited for transport either as gas or in aqueous solution, therefore one of its combinations with oxygen and a base, viz., a hypochlorite, is used. Hydrated oxide of calcium or slaked lime is the chief constituent of bleaching-powder. Usually the alkali manufacturers prepare bleaching-powder.

Preparation of Bleaching-Powder. Bleaching-powder is prepared on the large scale in the following manner:—In works where soda and chloride of lime are to be manufactured simultaneously, the chlorine is obtained by mixing the common salt to be converted into sulphate of soda by the action of sulphuric acid with peroxide of manganese, heat being applied.

The process is as follows:

$$\left.\begin{array}{l}\text{Common salt, } 2NaCl,\\ \text{Peroxide of manganese, } MnO_2,\\ \text{Sulphuric acid, } 2H_2SO_4\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Glauber's salt, } Na_2SO_4,\\ \text{Sulphate of manganese, } MnSO_4,\\ \text{Chlorine, } 2Cl, \text{ and } 2H_2O.\end{array}\right.$$

In some works chlorine is prepared by the reaction of hydrochloric acid and manganese, and sometimes with the addition of sulphuric acid. In the first instance only half the chlorine contained in the hydrochloric acid is given up, because the other half forms chloride of manganese; for—

$$\left.\begin{array}{l}\text{Manganese, } MnO_2,\\ \text{Hydrochloric acid, } 4ClH,\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Chlorine, } Cl_2,\\ \text{Manganic chloride, } MnCl_2,\\ \text{Water, } 2H_2O.\end{array}\right.$$

In the second instance all the chlorine contained in the hydrochloric acid is obtained—

$$\left.\begin{array}{l}\text{Manganese, } MnO_2,\\ \text{Hydrochloric acid, } 2ClH,\\ \text{Sulphuric acid, } H_2SO_4,\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Sulphate of manganese, } MnSO_4\\ \text{Chlorine, } Cl_2,\\ \text{Water, } 2H_2O.\end{array}\right.$$

As proposed by Clemm, a chloride of magnesium solution, as largely obtained at Stassfurt, may be employed by concentrating the solution to 44° B (= 1·435 sp. gr.,) and adding manganese, so that to 1 mol. of MnO_2, 2 mols. of $MgCl_2$ are taken. The cooled, solid mass, when exposed to the action of superheated steam at 200° to 300°, yields chlorine gas.

Preparation of Chlorine without Manganese. The following methods are selected as being the most scientific and interesting:—

1. Mac Dougal, Rawson, and Shanks's process, consisting in the decomposition of chromate of lime by hydrochloric acid, the result being the formation of chloride of chromium, chloride of calcium, and the evolution of free chlorine—

$$(2CaCrO_4 + 16HCl = Cr_2Cl_6 + 2CaCl_2 + 3H_2O + 6Cl).$$

158 parts of chromic acid yields 106 parts of chlorine. The chloride of chromium is again precipitated with carbonate of lime, and by ignition converted into chromate of lime. Only three-eighths of the chlorine contained in the hydrochloric acid is given up, while manganese yields one-half.

2. Schlösing's method consists in acting upon manganese with a mixture of hydrochloric and nitric acids, the degree of concentartion of the acids being so regulated by the addition of water that the mixture yields only chlorine, while nitrate of protoxide of manganese is formed; this salt being calcined yields manganese, peroxide, and nitric acid. The nitric acid aids the oxygen of the air in decomposing the hydrochloric acid. The nitrate of manganese begins to decompose at 150°, and the decomposition is completed at 175° to 180°, yielding much peroxide, in some cases even 93 per cent.

3. Vogel's method of decomposing chloride of copper by heat. 3 mols. of chloride yield 1 mol. of chlorine; according to Laurens the process is:—

$$2CuCl_2 = Cl_2 + Cu_2Cl_2.$$

The chloride in crystalline state is mixed with half its weight of sand, and heated in earthenware retorts to 200° to 300°, yielding chlorine gas, while the remaining protochloride of copper is re-converted into perchloride by the action of hydrochloric acid. Mallet has constructed a peculiar rotating apparatus for the decomposition of this salt, the same apparatus serving to prepare oxygen. 100 kilos of cupric chloride yield 6 to 7 cubic metres of chlorine gas.

4. Péligot's method. When 3 parts of bichromate of potassa and 4 parts of concentrated hydrochloric acid are gently heated, the fluid yields on cooling crystals of bichromate of chloride of potassium, KCl,CrO_3; at 100° this salt yields chlorine.

5. Dunlop's process is followed at Mr. Tennant's works, Glasgow. Sulphuric acid is made to act upon a mixture of 3 mols. of common salt, and 1 mol. of nitrate of soda, the result being the formation of chlorine and hyponitric acid. The latter is absorbed by passing the mixed gases through strong sulphuric acid.

6. Mr. Walter Weldon's process is performed by means of an apparatus comprising five vessels arranged at successive elevations, so that after having been pumped up to the highest of them, the liquor operated upon can afterwards descend to all the others by its own gravity. The lowest of these vessels is a well, which is furnished with a mechanical agitator. The slightly acid chloride of manganese liquor with which the process commences runs from the stills in which it is produced into this well, and is there treated with finely divided carbonate of lime, the action of which is facilitated by the energetic agitation. When the neutralisation of the free acid which is at first contained in this liquor and the decomposition of the sesquichloride of iron and sesquichloride of aluminium, which are also at first contained in it, are completed, the liquor is pumped up into settling tanks, placed nearly at the top of the apparatus, and known as the "chloride of manganese settlers." It now consists of a quite neutral mixed solution of chloride of manganese and chloride of calcium, containing in suspension considerable quantities of sulphate of lime, and small quantities of oxide of iron and alumina. These solid matters rapidly deposit in the chloride of manganese settlers, leaving the bulk of the liquor perfectly bright and clear, and of a faint rose-colour. The next step is to run off the clear portion of the contents of the settlers into a vessel immediately below, called the oxidiser. This is usually a cylindrical iron vessel about 12 feet in diameter, and about 22 feet deep. Two pipes go down nearly to the bottom of the oxidiser, a large one for conveying a blast of air from a blowing engine, and a smaller one for the injection of steam. The latter is for the purpose of raising the temperature of the contents of the oxidiser when necessary; for sometimes the chloride of manganese liquor reaches the oxidiser sufficiently hot—between 130° and 160° or 170° F. Immediately above the oxidiser is a reservoir containing milk of lime. The oxidiser having received a charge of clear liquor from the settlers, and this liquor having been heated up to the proper point, if it was not already hot enough, blowing is begun, and milk of lime is then run into the oxidiser as rapidly as possible, until the filtrate from a sample taken at a tap placed nearly at the bottom of the oxidiser, ceases to give a manganese reaction with solution of bleaching-powder. A certain quantity of milk of lime is then added, and the blowing continued until peroxidation ceases to advance. That point is usually attained when from about 80 to 85 per cent. of the manganese present has become converted into peroxide. The contents of the oxidiser are now a thin black mud, consisting of solution of chloride of calcium containing in suspension about 2 lbs. of peroxide of manganese per cubic foot, these 2 lbs. of peroxide of manganese being combined with varying quantities of protoxide of manganese and lime. This thin mud is now run off from the oxidiser into one or other of a range of settling tanks or "mud settlers," placed below it, and is there left at rest until it has settled as far as it will, usually until about one-half of its volume has become clear. The clear part is then decanted, and the remainder, containing about 4 lbs. of peroxide of manganese per cubic foot, is then ready to be used in the stills. There it reacts upon hydrochloric acid, liberating chlorine, with reproduction of exactly such a residual solution as was commenced with. With that solution the round of operations is begun again: and so on, time after time, indefinitely.

Apparatus for Preparing Chlorine. When hydrochloric acid and manganese are used, the apparatus is that delineated in Fig. 105. It consists of a large stoneware jar, A, provided with an opening, *a*, over which an air-tight cap is fitted when the apparatus is at work, and by which the jar is filled with manganese and acid; *b* is another opening fitted with a leaden or earthenware gas tube; *c* is a tube serving to run off the spent manganese liquor. B is a wooden box into which steam is admitted for the purpose of heating A and its contents sufficiently to promote the reaction between the hydrochloric acid and the manganese.

When chlorine is prepared from a mixture of common salt, sulphuric acid, and manganese, the apparatus is required to withstand more heat, and is therefore constructed entirely of metal. *a a*, Fig. 106, is a shallow iron pan, fitted with the tube *b* for the purpose of emptying the contents of the leaden cylinder, *d d*. This iron vessel serves as the lower part of the leaden cylinder, *d d*, the top of which is provided with an opening for a funnel syphon-tube for the introduction of the acid, and another opening, *f*, for the manganese. The entire apparatus stands on a flue leading from a furnace.

FIG. 105.

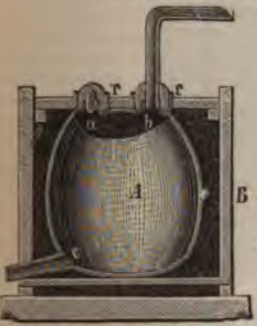
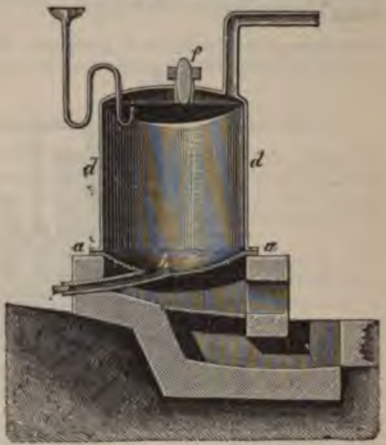
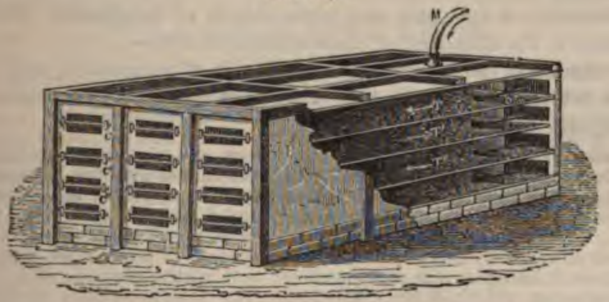


FIG. 106.



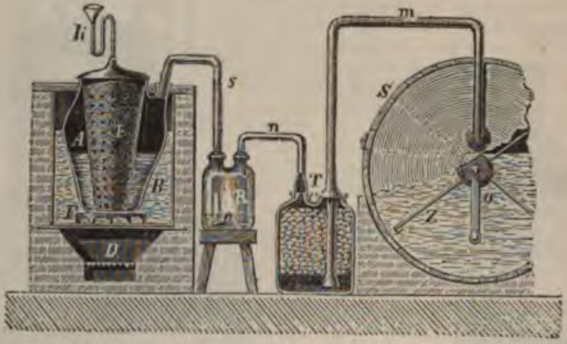
Condensing Apparatus. The chlorine passes from the generator through the tube, M, Fig. 107, into a room constructed of large blocks and slabs of sandstone joined by means of asphalt cement, or a mixture of coal-tar and fire-clay. Sometimes the room is built of bricks laid in a similar cement, the interior being lined with asphalt; leaden chambers also are used for this purpose. The room is fitted with several shelves upon which slaked lime is placed in layers of three to four inches and more in thickness. The chlorine gas is readily absorbed heat being evolved. Care is to be taken that the temperature does not exceed 25°, because then chlorate of lime is formed; this is prevented by admitting the gas slowly. As soon as the absorption ceases, the bleaching-powder is removed with rakes from the shelves, and fresh lime introduced. Frequently the chloride of lime is somewhat diluted by an admixture of slaked lime.

FIG. 107.



When it is desired to prepare a solution of chloride of lime, the apparatus shown in Fig. 108 is employed. Two or four earthenware vessels, A, about 2 hectolitres capacity, are placed in the leaden trough, B, the bottom of which is protected by a cast-iron plate and a stoneware slab, F, from the direct action of the fire at D. B represents a concentrated solution of chloride of calcium serving the purpose of a bath, such a solution boiling at 179·5°. By the syphon funnel, K, the hydrochloric acid is poured into A. I is a perforated cistern filled with manganese. S is the leaden gas tube. The chlorine being first washed in R, passes through *n* into T, filled with pieces of manganese, to decompose any vapours of hydrochloric acid carried over, and lastly, the chlorine passing through *m* reaches the absorption vessel, S. This vessel is a lead-lined wooden cask, fitted with an axle bearing spokes to which are fastened gutta-percha floats. The bearing and plummer-blocks of the axle are made of guaiacum wood and ebonite. The axle, *o*, gears with a suitable motive power, the purpose being to keep the milk of lime in continuous motion while the gas is being admitted.

FIG. 108.



The chlorine gas enters above the level of the fluid, which is kept constantly stirred, to assist in the absorption. From the vessel wherein the absorption takes place a small tube leads into another vessel filled with water to a depth of 18 to 24 centims.; a tube fitted to this vessel leads into the open air to convey away any unabsorbed chlorine. As in the preparation of solid chloride of lime, it is here necessary to guard against an increase in temperature and also saturation; Schlieper has proved that too concentrated solutions evolve oxygen, while too dilute solutions yield chlorate of lime.

Utilisation of the Chlorine Production Residues.

As the chlorine required for the preparation of chloride of lime is generally obtained by the aid of manganese and hydrochloric acid, the residues consist chiefly of free acid and protochloride of manganese. The principal suggestions as to the utilisation of these substances are:—

α. Those aiming at the regeneration of peroxide of manganese; and

β. Those not proceeding with this view. The former are of course the more important.

Dunlop's Process. This process is one of the oldest and the best, excepting perhaps, Balmain's, in which the chloride of manganese is neutralised with the ammoniacal water of gas-works, the supernatant liquor being employed for preparing sal-ammoniac, while the precipitate is ignited in a reverberatory furnace and converted into peroxide of manganese. Dunlop's process, as practised at Tennant's works at Glasgow, is based upon the fact, first observed by Forchhammer, that carbonate of manganese, when heated to 260°, is converted into peroxide of manganese; that is, the carbonic acid is driven off, and the compound, $2MnO_2+MnO$, obtained. The process consists in the following operations:—

1. Conversion of the chloride of manganese into carbonate of manganese.
2. Conversion of the carbonate into peroxide of manganese.

To the chlorine preparation residues, when they have become clear, either chalk or milk of lime is added to neutralise the excess of acid and precipitate the oxide of iron. This precipitate having settled, the clear liquid, a rather pure solution of protochloride of manganese, is poured into shallow troughs and intimately mixed with finely powdered chalk. The magma thus formed is transferred for further decomposition to a large cast-iron trough, 27 metres long by 3 metres wide. Parallel to the length of this vessel, a stout wrought-iron axle is carried, to which are fitted cast-iron branches serving as stirrers.

The axle passing through stuffing boxes at each end of the trough, gears with a motive power, whereby the stirrers are caused to keep the chalk constantly suspended in the manganese solution. High-pressure steam is conveyed into the trough and aids decomposition. The carbonate of manganese obtained is freed by washing from chloride of calcium, and having been well drained, is calcined in a peculiarly constructed furnace, in which the carbonate is first dried on a higher stage, and then is transferred to a lower and hotter stage, where oxidation is commenced. The oxidation is completed at the lowest stage of the furnace, to which plenty of air is admitted. The fire-place is constructed to admit of the regulation of the heat with great nicety, because too high a temperature would cause the formation of protosesquioxide, and too low a temperature would leave the carbonate undecomposed.

Gatty's Process. In this process the residues are converted into nitrate of manganese, which is next decomposed by heat. The residues are evaporated to the consistency of a syrup, and mixed with nitrate of soda:—

To 76 kilos. of protochloride of manganese
and to 95 kilos. of sulphate of manganese } 106 kilos. of nitrate of soda are taken.

The mixture is dried, and then heated to a dull red heat in an iron retort, the fumes of nitric acid given off being used in the manufacture of sulphuric acid. The residue in the retort consists, according to the salt of manganese employed, of peroxide of manganese and chloride of sodium or sulphate of soda; it may be lixiviated with water to obtain the peroxide of manganese in a pure state if sulphate of soda is present.

Hofmann's Process. The processes of regenerating manganese by the application of soda waste are more important than the preceding. In Hofmann's process the protochloride of manganese is, by the addition of the yellow ley obtained from the lixiviation of soda waste converted into sulphuret of manganese. The precipitate, consisting of—

Sulphuret of manganese	55·00
Sulphur	40·00
Protoxide of manganese	5·00
	100·00

is dried and calcined, the sulphurous acid given off being led into the sulphuric acid chambers. The remaining residue, consisting of—

Sulphate of manganese	44·5
Peroxide of manganese	18·9
Protoxide of manganese	36·6
	100·0

is next mixed with nitrate of soda and heated to 300°, yielding sulphate of soda and nitrate of manganese, the latter, however, being at once decomposed into peroxide of manganese and hyponitric acid:—

$$\alpha.\ MnSO_4 + 2NaNO_3 = Mn(NO_3)_2 + Na_2SO_4;$$
$$\beta.\ Mn(NO_3) + MnO_2 + 2NO_2.$$

After the mass has cooled, the sulphate of soda is removed by lixiviation, the residue yielding a material free from iron, and according to the inventor, equal to native manganese.

Weldon's Process. To the residue, consisting of protochloride of manganese, are first added for every molecule of that salt 2 molecules of hydrate of lime. Into this magma, consisting of hydrate of protoxide of manganese, hydrate of lime, and chloride of calcium, air is forced, the effect being that the manganese is rapidly higher oxidised, and forms calcium-manganite ($CaMnO_3$, or MnO_2,CaO), which, having subsided, and the supernatant chloride of calcium solution being run off, is ready for chlorine making by the addition of hydrochloric acid. The same process is repeated, and even a change of vessels is not required. (See p. 216.)

Other Methods of Utilising the Residues. β. Utilisation of the residues without regeneration of the peroxide of manganese. M. Schaffner, at Aussig, precipitates the protochloride of manganese with lime, dries the precipitate, and calcines it in a reverberatory furnace, obtaining protosesquioxide of manganese, employed with iron ore in the blast furnace. The solution of chloride of calcium simultaneously obtained is precipitated by sulphuric acid, yielding the material known as *annaline;* that is to say, the gypsum used in paper manufacture. In the process of soda-making from sulphuret of sodium and iron, as suggested by Malcherbe and improved upon by Kopp, for the oxides and carbonate of iron, the corresponding manganese compounds may be substituted. Carbonate of manganese may be used to convert sulphuret of sodium into soda, and may also serve for the preparation of permanganates. A. Leykauf suggests that the residues of chlorine manufacture should be employed to form a violet-coloured paint, known as Nüremberg-violet, a compound of ammonia, oxide of manganese, and phosphoric acid. In England the residues are frequently employed in the purification of coal-gas and as disinfectants.

Theory of the Formation of Bleaching-Powder. When chlorine gas and slaked lime (hydrated oxide of calcium, CaH_2O_2) are brought in contact, a portion of the oxygen of the lime combines with the chlorine, forming hypochlorous acid, which, combining with the undecomposed lime, forms hypochlorite of lime, while another equivalent of chlorine combines with the deoxidised lime (calcium) forming chloride of calcium:—

$$\left.\begin{matrix}\text{Hydrate of lime, } 2CaH_2O_2,\\ \text{Chlorine, } 2Cl_2,\end{matrix}\right\}\text{ yield }\left\{\begin{matrix}\text{Hypochlorite of lime, } Ca\,(Clo)_2,\\ \text{Chloride of calcium, } CaCl_2,\\ \text{Water, } 2H_2O.\end{matrix}\right.$$

This bleaching-powder consists in 100 parts of:—

Hypochlorite of lime	49·31
Chloride of calcium	38·28
Water	12·41
	100·00

or of—

Chlorine	48·90
Lime	38·69
Water	12·41
	100·00

A bleaching-powder of this theoretical composition does not and cannot occur in the trade; a good sample, containing 26·52 per cent. of active chlorine was composed as follows:—

Hypochlorite of lime	26·72
Chloride of calcium	25·51
Lime	23·05
Water of composition and moisture	24·72
	100·00

This analysis may be more intelligible by the following arrangement:—

Hypochlorite of lime	26·72
Active chloride of calcium	20·72
Excess of chloride of calcium	4·79
Hydrate of lime	30·46
Water of composition and moisture	17·31
	100·00

According to Dr. Fresenius (1861), bleaching-powder is a mixture of 1 molecule of $Ca(ClO)_2$ and 2 molecules of basic chloride of calcium, $CaCl_2,2CaH_2O_2+2H_2O$.

Properties of Bleaching-Powder. Bleaching-powder is a white, rather moist powder, consisting of hypochlorite of lime, chloride of calcium, and excess of slaked lime. 10 parts of water dissolve the bleaching material, leaving the excess of lime; the chlorine contained in the chloride of calcium also acts as a bleaching agent, as on adding an acid to the bleaching-powder the hypochlorous acid set free reacts upon the hydrochloric acid evolved from the chloride of calcium, forming water and chlorine:—

$$\Big(\begin{matrix}Cl\\H\end{matrix}\Big\}O+\begin{matrix}H\\Cl\end{matrix}\Big\}=\begin{matrix}H\\H\end{matrix}\Big\}O+\begin{matrix}Cl\\Cl\end{matrix}\Big\}\Big)$$

The bleaching power of chloride of lime does not come immediately into play unless an acid is added; this property is turned to account in the producing of white patterns upon fabrics dyed turkey-red, by printing the pattern in a thin paste of tartaric acid, the fabric being afterwards immersed for a few minutes in a solution of hypochlorite of lime. Instead of employing acids for setting the chlorine free from chloride of lime, sulphate or chloride of zinc may be substituted, the result being that gypsum and oxide of zinc are precipitated, while hypochlorous acid remains in solution.* The various industrial uses of bleaching-powder have already been mentioned. Chloride of lime, as bleaching powder is generally termed in this country, is sometimes used for the preparation of oxygen, 1 kilo. (of the formula $Ca(ClO)_2$), yielding 132·2 grms. = 92·4 litres of oxygen.

Chlorimetry. As the value of a sample of chloride of lime depends upon the quantity of of the really active chlorine and hypochlorous acid it contains, methods have been devised for ascertaining with a greater or less degree of accuracy the quantity of these active agents. Formerly the test was the discolouration of a certain quantity of indigo solution by a certain quantity of bleaching-powder solution, as compared with the action of chlorine upon indigo, but it is clear that this method could not yield accurate results.

Gay-Lussac's Chlorometric Method. This eminent *savant* makes use of the oxidising action of chloride of lime upon arsenious acid, a volume of dry chlorine gas dissolved in water being employed. The solution of chlorine is poured into a graduated tube divided into 100 parts, each of these divisions corresponding to one-hundredth of chlorine. A solution of arsenious acid in dilute hydrochloric acid is also prepared, the strength of the solution being such that equal bulks of the two liquids suffer mutual decomposition:—

$$\left.\begin{array}{l}\text{Arsenious acid, } As_2O_3,\\ \text{Water, } 2H_2O,\\ \text{Chlorine, } 2Cl_2,\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Arsenic Acid, } As_2O_5.\\ \text{Hydrochloric acid, } 4ClH\end{array}\right.$$

Water is decomposed; its oxygen combines with the arsenious acid, forming arsenic acid, while the hydrogen combines with the chlorine. Usually 1 litre of dry chlorine gas is dissolved in 1 litre of distilled water. The normal solution of arsenious acid is so prepared that it is entirely decomposed by the chlorine water to arsenic acid. The test is carried out as follows:—Take 10 grms. of the sample, and triturate with distilled water, adding sufficient of the latter to make up a litre. Next take, by means of a graduated pipette, 10 c.c. of the arsenious acid solution, and pour it into a beaker, adding a drop of indigo solution to impart a faint colour; next add, by means of a burette, sufficient of the bleaching powder solution to cause the colour nearly to disappear, then add more of the indigo solution, and again bleaching-powder solution, until the fluid becomes quite colourless. The normal arsenious acid solution is prepared by dissolving 4·4 grms. of this acid in 32 grms. of hydrochloric acid, the liquid to be diluted to 1 litre. If 10 grms. of bleaching-powder contain 1 litre of chlorine gas, it is of 100 degrees strength.

Penot's Test. Penot has modified Gay-Lussac's method in the following particulars:—For the arsenious acid solution he substitutes arsenite of soda, and for the indigo solution a colourless iodised paper, which is turned blue by the smallest quantity of free acid. The paper is prepared in the following manner:—1 grm. of iodine, 7 grms. of carbonate of soda, 3 grms. of starch, and ¼ litre of water are mixed. When the solution becomes colourless, it is diluted to ½ a litre; in this fluid white paper is soaked. The arsenical fluid is prepared by dissolving 4·44 grms. of arsenious acid, and 13 grms. of crystallised carbonate of soda in 1 litre of water. This solution is poured by means of a burette into the solution of the chloride of lime intended to be tested (10 grms. of the sample to 1 litre), the completion of the reaction being known by the paper remaining uncoloured. Mohr, again, has modified this process, in not however very essential particulars.

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* Explosions have occurred from bleaching-powder being kept in too tightly closed vessels, due to spontaneous decomposition, ($Ca(ClO)_2 + CaCl_2 = 2CaCl_2 + O_2$). As a prevention it is suggested that the powder should be ground, packed in casks, and strongly pressed into a hard mass.

Dr. Wagner's Method. This test, discovered in 1859, is the so-called *iodometrical method*, and is based upon the fact that a solution of chloride of lime separates the iodine from a weak (1 to 10) and slightly acidified iodide of potassium solution, the iodine being quantitatively estimated by means of hyposulphite of soda:—

$$\left.\begin{array}{l}\text{Iodine, } 2I,\\ \text{Hyposulphite of soda, } 2Na_2S_2O_3+5H_2O,\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Iodide of sodium, } 2NaI,\\ \text{Tetrathionate of sodium, } Na_2S_4O_6,\\ \text{Water, } 5H_2O.\end{array}\right.$$

The test is thus executed:—100 c.c. = 1 grm. of bleaching-powder solution, obtained by dissolving 10 grms. of chloride of lime in 1 litre of water, are mixed with 25 c.c. of solution of iodide of potassium acidified with dilute hydrochloric acid. The ensuing clear, deep brown coloured solution is treated with hyposulphite of soda solution until quite colourless. The hyposulphite of soda solution is composed of 24·8 grms. of that salt to 1 litre of water; 1 c.c. of this solution neutralises 0·0127 grms. of iodine and 0·00355 grms. of chlorine.

Chlorometrical Degrees. The strength of bleaching-powder is indicated in England, Russia, America, and Germany by degrees corresponding to the percentage of active chlorine; but in France the degrees denote the number of litres of chlorine gas at 0° and 760 millimetre Bar., which 1 kilo. of bleaching-powder can evolve. The following table compares the chlorometrical degrees of France and England:—

French.	English.
63	20·02
65	20·65
70	22·24
75	23·83
80	25·42
85	27·01
90	28·60
100	31·80
105	33·36
110	34·95
115	36·54
120	38·13
125	39·72
126	40·04

The percentage is calculated by multiplying the French degrees by the coefficient 0·318, a litre of chlorine gas = 35·5 criths, weighing 3·18 grms.

Alkaline Hypochlorites. A solution of hypochlorite of potassa is known in commerce under the name of *Eau de Javelle*, while the corresponding soda solution is known as *Eau de Labarraque;* these solutions are prepared by passing chlorine gas into a solution of either caustic (1), or carbonated (2) alkali:—

(1). $2NaOH + Cl_2 = NaOCl + NaCl + H_2O$;

(2). $2Na_2CO_3 + Cl_2 + H_2O = NaOCl + NaCl + 2NaHCO_3$;

or by exhausting bleaching-powder with water, and precipitating the solution with sulphate or carbonate of soda solution, sulphate or carbonate of lime being thrown down, while the hypochlorite and chloride of the alkali remain in solution.

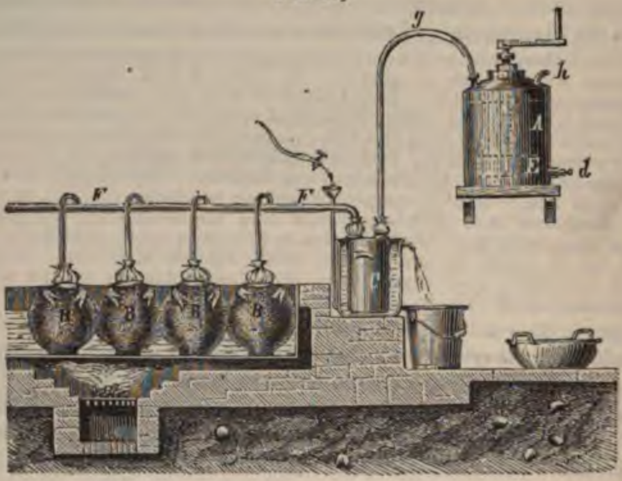
Hypochlorite of aluminium, or Wilson's bleaching powder, is obtained by mixing chloride of lime solution with sulphate of alumina; its action is by evolving oxygen, leaving chloride of aluminium in solution. Hypochlorite of magnesia (Ramsay's or Grouville's bleaching liquor) is obtained by adding sulphate of magnesia to a solution of bleaching-powder; the result is the formation of a very energetic bleaching compound, which, especially for the purpose of bleaching finely-woven-fabrics, as muslins, &c., is preferable to chloride of lime on account of the absence of caustic lime. Varrentrapp's bleaching salt, or hypochlorite of zinc, is another energetic bleaching compound obtained by treating a solution of chloride of lime with sulphate of zinc, the result being the precipitation of sulphate of lime, while hypochlorite of zinc remains in solution; chloride of zinc may be employed, but, of course, the solution then retains chloride of calcium. Hypochlorite of baryta is sometimes used, hypochlorous acid being obtained by the addition of very dilute sulphuric acid.

Chlorate of Potassa. This salt ($KClO_3$) consists in 100 parts of 38·5 of potassa and 61·5 of chloric acid; its crystals are rhombic and tabular in form. It formerly was prepared by passing chlorine gas into a concentrated solution of carbonate of potassa, the result being the formation of chlorate of potassa and chloride of potassium. As the chlorate is the least soluble it crystallises first, while by evaporation the mother-liquor yields chloride of potassium. The chlorate is then washed with cold water, and purified by re-crystallisation. 100 kilos. of carbonate of potassa yield in this manner 9 to 10 kilos. of the chlorate. At the present day, however, chlorate of potassa is prepared by a method, the suggestion of the late Dr. Graham. Chlorine is caused to act at a high temperature upon milk of lime, with the result of the formation of chlorate of lime and chloride of calcium, the chlorate of lime being afterwards decomposed by chloride of potassium. The method by which chlorate of potassa is prepared on the large scale according to this plan is the following:—1 mol. of chloride of potassium and 6 mols. of hydrate of lime, having been mixed with water, are submitted to the action of chlorine gas; the solution yields on evaporation crystallised chlorate of potassa, while chloride of calcium remains.

This operation is carried on by the aid of the apparatus illustrated in Fig. 109. B B are earthenware jars, placed in a chloride of calcium bath, and filled with a mixture for evolving chlorine gas. This gas is conveyed through the leaden tube, F F, to the vessel, C, which is placed in cold water for the purpose of condensing any aqueous vapours. From C the gas passes through the leaden tube *g* into the absorption vessel, A, in which the mixture of lime and water has been placed. E is an iron stirrer covered with lead, *h*, a portion of the tube for carrying off the non-absorbed chlorine; *d*, a tube closed with a plug during the operation, and intended for tapping off the contents of the vessel. The milk of lime is poured into the vessel at 50° to 60° C., while sometimes steam is injected for the purpose of keeping up the temperature, which rises as soon as the reaction commences nearly to the boiling-point. A small quantity of hypochlorite of lime is always formed. As soon as no more chlorine is absorbed the fluid is tapped off into a lead-lined tank, and after the suspended matter has been deposited, is syphoned over into a leaden evaporating pan and concentrated to 25° to 30° B., any hypochlorite of lime being thus converted into chlorate. To the evaporated and concentrated solution there is added a hot solution of chloride of potassium, after which the evaporation is continued to crystallisation. According to theory, 2¼ parts of lime require 1 part of chloride of potassium;

in practice, however, to every 3 parts of lime 1 part of chloride of potassium is taken. Old chloride of lime which has become unfit for bleaching purposes may be utilised by first preparing chlorate of lime, and boiling a solution of this chlorate, adding to the concentrated fluid chlorate of potassium to obtain chlorate of potassa. Chlorate of potassa is not altered by exposure to air, is soluble in 16 parts of water at 15·8°, in 8 parts of water at 35°. and in 1·6 parts of water at 100°. On being heated to fusion, this salt yields oxygen; if incautiously rubbed in a mortar with combustible substances, as sulphur or phosphorus, violent explosions will ensue. 1 kilo. of the chlorate yields, when heated with either 0·5 kilo. of manganese or 1 kilo. of oxide of iron, or, better still, with a small quantity of oxide of copper (see "Chemical News," vol. xxiv., p. 85), 391·2 grms. = 273·5 litres of oxygen. Chlorate of potassa is chiefly employed in pyrotechny for the preparation of white powder, as an ingredient in the explosive mixture for the cartridge of needle-guns, as an oxidising agent in calico-printing, and in the preparation of aniline black. Perchlorate of potassa (KCl_2O_4) is now more frequently used in pyrotechny, being less dangerous to manipulate, and owing to the large quantity of oxygen, emitting more intense light.

FIG. 109.



ALKALIMETRY.

Alkalimetry. The potash met with in commerce, no matter from what source it is obtained, is always a mixture of carbonate of potassa with other salts of potassa and soda; and again the carbonate of soda of commerce is a mixture of the carbonate with other soda salts, chiefly sulphate and chloride. The value of either of the salts of course depends chiefly upon the quantity of pure carbonate present in a given sample. The quantitative determination may be effected by either of two rapid, yet sufficiently accurate, methods:—

a. The estimation of the quantity of acid required to neutralise the alkaline carbonate;

b. The determination of the quantity of carbonic acid evolved by the addition of a strong acid.

It is clear that these methods can be applied only when no other than the alkaline carbonate is present.

Volumetrical Method. This method, invented by Descroizilles and improved by Gay-Lussac, is based upon the measurement of the quantity of sulphuric acid required to expel the carbonic acid from a certain quantity of carbonate of potassa, this measurement giving the quantity of pure salt. The best sulphuric acid is prepared by mixing 100 grms. of pure sulphuric acid, sp. gr. = 1·842, with 1000 grms. = 1000 c.c. = 1 litre of distilled water; or, instead of weighing the acid, 54·268 c.c. may be mixed with a litre of water. 50 c.c. of this normal acid solution suffice for converting 4·807 grms. of potassa into sulphate of potassa. The burette of 50 c.c. capacity and graduated to half a c.c., is filled with test-acid; next 4·807 grms. of potassa are weighed out and dissolved in boiling water. Some litmus tincture is now added, and the test-acid poured from the burette into the potash solution until the colour is a wine-red. Supposing 60 demi-c.c. to have been used in saturating the potash, and deducting ½ c.c. for possible excess, the sample contains potash of 59½°. The quantity of potassa per cent. is calculated by multiplying the quantity found by 1·47. Potash of 50° contains 50 × 1·47 = 75·5 per cent. carbonate of potassa.

Mohr's Method. Mohr substitutes for the sulphuric acid crystallised oxalic acid—

$$(C_2H_2O_4,2H_2O = 126;\ \tfrac{1}{2}\text{ mol.} = 63),$$

because:—1. It is as strong as, and similar to, sulphuric acid in its action upon litmus; 2. Being neither deliquescent nor efflorescent, it can be readily weighed off in a dry state with accuracy; 3. Its aqueous solution is not liable to become mouldy by keeping, as are the solutions of citric and tartaric acids; 4. It is not volatile when in hot water. To prepare the normal acid liquor, 63 grms. of oxalic acid are dissolved in a litre of water; on the other hand, there is prepared a corresponding solution of caustic potassa so titrated that, on being mixed with an equal bulk of the acid solution, the last drop of the alkaline solution restores the blue colour of the previously reddened litmus, provided the liquor does not contain carbonic acid in solution. For alkalimetric purposes 6·911 grms. of potash or 5·32 grms. of soda are weighed out, these quantities being equal to $\frac{1}{20}$ molecule, and as the test-acid contains in 1000 c.c. ½ molecule of oxalic acid, 100 c.c. will exactly neutralise the quantity of alkali. Some litmus tincture is mixed with the alkaline solution, to which the oxalic acid solution is added in a slight excess (5 to 6 c.c.), the solution being boiled to expel all the carbonic acid. There is now added by means of a pipette divided into tenths-c.c., just sufficient caustic alkali to turn the litmus blue; the number of c.c. of alkali solution employed is deducted from the number of c.c. of acid solution employed, the difference giving the percentage of pure carbonate of potassa contained in the sample. For instance, if 3·45 grms. of the potash = $\frac{1}{40}$ molecule, require 36 c.c. of the acid and 3 c.c. of the alkaline liquor, there will be 33 c.c. test-acid = 66 per cent. carbonate of potassa, as, instead of $\frac{1}{20}$ mol., $\frac{1}{40}$ mol. having been employed, the number of c.c. of test-acid must be doubled.

These instances of alkalimetric processes will suffice for the purposes of elucidation, but the reader will find fuller explanations in works on volumetric analysis. However, it is still to be observed that as potash is a very hygroscopic substance, it is necessary to estimate the water it contains, or at least to dry the sample. As 6·29 grms. of commercial potash and 4·84 grms. of soda contain when pure exactly 2 grms. of carbonic acid, every 2 centigrms. loss equals 1 per cent. of carbonate. Supposing the loss of weight to amount to 164 centigrms. the sample will contain $\frac{164}{2}$ = 82 per cent. of carbonate of potassa; for scientific purposes it would answer to say that such a sample consists in 100 parts of:—

Carbonate of potassa	82
Foreign salts	8
Water	10
	100

For commercial purposes, however, at least abroad, the value (*titre*) of a sample of potash expresses the percentage of anhydrous salt; for instance, by potash at $\frac{60}{100}$, is meant potash containing 60 per cent. of real carbonate when in a dry state. But if, by having taken up moisture, 100 lbs. have increased in weight to 105 or 109 lbs., the expression $\frac{60}{105}$ or $\frac{60}{109}$ is equivalent to saying that the amount of money that would buy $\frac{60}{100}$ of dry material will also buy $\frac{60}{105}$ and $\frac{60}{109}$ of the moist salt; the purchaser, therefore, does not pay for water, and all that he has to do is to ascertain the quantity of water present in the sample. In France the quantity of soda contained in a sample is usually expressed in degrees indicating the percentage of carbonate of soda, and in England the percentage of caustic soda; thus, as 100 parts of carbonate of soda contain 58·6 of soda and 41·4 of carbonic acid, it follows that—

80° French are equal to 46·9° English.
86° „ „ „ 50·5°
96° „ „ „ 52·8°

Gruneberg's Method of Estimating the Value of Potash.

In the preceding methods of testing potash no notice is taken of the soda contained in the samples, nor is the quality of the potassa salts considered. It is clear that these determinations require a full analysis, which, by Grüneberg's method, is executed in the following manner:—The carbonate of potassa is estimated by Gay-Lussac's method, the chlorine by the aid of nitrate of silver, the sulphuric acid by nitrate of lead, and the quantity of any free caustic potassa is determined by means of tartaric acid. All the chlorine is calculated as chloride of potassium, all the sulphuric acid as sulphate of potassa, and the rest of the potassa as carbonate; the quantity thus found is deducted from that found alkalimetrically, and the remainder is calculated to be carbonate of soda in the proportion of 69·1 to 53·0.

AMMONIA AND AMMONIACAL SALTS.

Ammonia.

Ammonia occurs in the atmosphere. Ammoniacal salts are met with in a few minerals and in volcanic districts. But the bulk of the ammonia and ammoniacal salts industrially used, is obtained from the dry distillation of coals, bones, and animal substances, also by the distillation of lant (stale urine), by the action of steam on some cyanogen compounds, and as a product of the blast-furnace process.

The following sources of ammonia are technically available:—

α. Inorganic sources.
- 1. Native carbonate of ammonia,
- 2. Preparation of ammoniacal salts with boracic acid,
- 3. Volcanic sal-ammoniac,
- 4. Ammonia from nitric acid in the purifying of caustic soda,
- 5. „ „ deutoxide of nitrogen and nitrous acid,
- 6. „ „ the nitrogen of the air,
- 7. „ „ certain cyanogen compounds.

β. Organic sources.
- 8. Coals yield ammonia:—
  - *a.* By the dry distillation for the purpose of gas manufacture,
  - *b.* By the coking of coals,
  - *c.* By the use of coals as fuel;
- 9. Ammonia from lant,
- 10. „ „ the dry distillation of bones,
- 11. „ „ beet-root juice.

Ammonia, NH_3, consists of 1 volume of nitrogen and 3 volumes of hydrogen, condensing to 2 volumes of ammonia gas, a colourless gas of a peculiar and well-known odour and sharp biting taste. At 15° water absorbs 727, and at 0° 1050 times its own bulk of this gas, the solution being known as liquid ammonia, or spirit of sal-ammoniac, the sp. gr. of which is 0·824 (=31·3 per cent. NH_3). Usually, however, a weaker and more stable liquid ammonia is prepared for pharmaceutical and technical purposes, having a sp. gr. = 0·960 (= 9·75 per cent. NH_3). The following table shows the specific gravity of liquid ammonia, and the percentage of ammonia contained:—

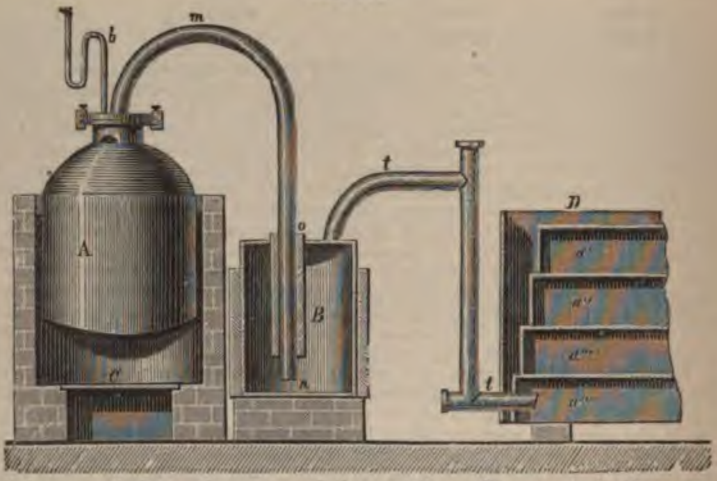
Sp. gr.	NH_3 per cent.	Sp. gr.	NH_3 per cent.
0·875	32·50	0·959	10·0
0·824	31·30	0·961	9·5
0·900	26·00	0·963	9·0
0·905	25·39	0·965	8·5
0·925	19·54	0·968	8·0
0·932	17·52	0·970	7·5
0·947	13·46	0·972	7·0
0·951	12·00	0·974	6·5
0·953	11·50	0·976	6·0
0·955	11·00	0·978	5·5
0·957	10·50		

Ammonia gas is very soluble in alcohol. The *spiritus ammoniaci caustici Dzondii* of the Prussian Pharmacopœia is a solution of ammonia gas in alcohol of 0·820 sp. gr.; the ammoniacal solution containing 10 per cent. of real NH_3, and having a sp. gr. of 0·808 to 0·810. The *liquor ammonii vinosus* is a mixture of 1 part of liquid ammonia (at 10 per cent. NH_3) and 2 parts of strong alcohol. Liquid ammonia is industrially employed for the extraction of the lichen (orchil) pigments, in the preparation of carmine, the manufacture of snuff, the purifying of coal-gas, for the removal of carbonic acid and sulphuretted hydrogen, for the saponification of fats, the preparation of ferrocyanide of potassium according to Gelis's plan with the aid of sulphide of carbon, for the extraction of chloride of silver from its ores, as antichlor in bleach-works, and in the manufacture of pigments and dyes. As regards the use of liquid ammonia for the extraction of copper from pyritical ores, Barruel stated (1852) that the copper might be dissolved by simply impregnating finely pulverised ore with liquid ammonia, and forcing air through the mixture, the metal being obtained as black oxide of copper after the ammonia is distilled off. This process, however, has not been found to answer on the large scale. The researches of von Hauer, Schönbein, Tuttle, and others, have proved that the oxidation of the ammonia is simultaneous with the oxidation of the copper, and that the nitrous acid thus formed is the active agent. Moreover, the experiments of Liebig and Way have proved that even if the operation were carried on in air-tight vessels, the ammonia could not be entirely recovered, owing to the fact that the ores absorb ammonia, and render it insoluble, thereby preventing its action on the copper. But if the copper ore be tolerably pure malachite or lazulite, only containing lime or carbonate of that base, liquid ammonia may be successfully employed. Liquid ammonia is used in Carré's ice-making machine. The *rationale* of this machine is that ammoniacal gas being expelled by heat from its aqueous solution, is again condensed and liquefied by pressure and cooling; the retort in which the ammonia is heated being next cooled by water, a vacuum is created, and as a consequence the ammonia contained in the condenser volatilised, returned to the retort, and again taken up by the water present. On again resuming the gaseous state, the ammonia absorbs a great amount of heat, causing a diminution in temperature sufficient to freeze water. Carré's ice-machine yields 10 kilos. of ice for every kilo. of coal consumed as fuel. Although Fournier has suggested that ammoniacal gas might be usefully employed in testing the joints of gas-fittings in houses, this is more readily effected by the use of a hand air-pump. The application of ammonia as a source of motive power has been tried, but it is not at present likely that it will supersede steam.

Preparation of Liquid Ammonia. By decomposing with caustic lime either chloride of ammonium or sulphate of ammonia, ammoniacal gas is set free, and can be absorbed by water, care being taken that the lime is in excess. When carbonate of ammonia is prepared on the large scale by sublimation of a mixture of chalk and sal-ammoniac, a large quantity of ammoniacal gas, 14 parts for each 100 parts of carbonate of ammonia, is obtained and may be utilised. Wagner has been the first to observe that the technical preparation of liquid ammonia might be combined with the preparation of baryta-white by precipitating a solution of sulphate of ammonia with caustic baryta-water; the clear supernatant liquor will be a solution of caustic ammonia.

The preparation of liquid ammonia on the large scale is effected by means of the apparatus shown in Fig. 110. A is a cast-iron distilling vessel placed in a brickwork furnace. To the neck of the vessel is fitted a lid secured to the flange by means of bolts and nuts, and luted with red-lead. The lid carries an iron tube, *m*, leading to the wash vessel, B, of wrought-iron. This vessel is surrounded by cold water contained in a wooden tank, and is provided with a wide tube, *o*, through which *m* passes. The wash vessel is filled with only so much water as will close the tubes *n* and *o* hydraulically, as during the operation a large quantity of water is distilled over from A. 100 parts of slaked lime are mixed with a sufficient quantity of water to form a thin milk of lime, which is poured into A; the lime solution having become quite cold, there is added 100 parts of pulverised sal-ammoniac or sulphate of ammonia, being thoroughly mixed by stirring with an iron rod. The lid being screwed on A, the fire is lighted in C; the mercurial gauge, *b*, shows the course of the operation. The ammoniacal gas proceeds from the wash vessel, B, through the tube *t* into the condensing apparatus, D, invented by Brunnquell, and highly useful for this and for similar purposes where it is desired to work under a low pressure. This apparatus consists of a large tank or box in which four shallow boxes, *a*′, *a*″, *a*‴, *a*⁗, are placed bottom upwards, the sides of the boxes being perforated with small slits. The outer tank is filled with water. When ammoniacal gas enters through *t* into *a*⁗, it forms a large bubble, similar to an air bubble under ice, and reaching one of the small slits rises into *a*‴, and so on, the bubble becoming smaller and smaller as the water gradually absorbs the gas. The box or tank, D, is placed in a large tank, not represented in the cut, filled with cold water constantly renewed. The still, A, is of sufficient capacity to contain 20 kilos. of sulphate of ammonia and 80 litres of water. The operation is continued until the bottom of the still becomes red-hot. The water contained in B is used at a subsequent operation for mixing with the lime. The preparation of liquid ammonia directly from gas liquor, the ammoniacal water of gas works, will be mentioned presently. The application of the property of chloride of calcium to absorb ammonia and deliver it up on the application of heat has been attempted industrially by Knab for the storing up of ammonia. Strong liquid ammonia only contains 25 per cent. NH_3, and Knab's preparation 50 per cent.; as regards transport this may not be an uninteresting fact, but chloride of calcium is a very deliquescent salt.

FIG. 110.



Inorganic Sources of Ammonia.

Before proceeding to describe the preparation of ammoniacal salts from bones, coals, lant, &c., we must first enumerate the inorganic sources of ammonia of industrial importance.

1. Native carbonate of ammonia, met with in large quantities in the guano deposits of South America, was imported into Germany as a commercial article in 1848. On being analysed this substance was found to consist of—Ammonia, 20·44; carbonic acid, 54·35;

water, 21·54; and insoluble matter, 21·54 parts. It is, therefore, a bicarbonate of ammonia $(NH_4)HCO_3$.

2. The preparation in Tuscany of native sulphate of ammonia as a by-product of the preparation of boracic acid has recently become important. The suffioni contain, in addition to boracic acid, sulphates of potassa, soda, ammonia, rubidium, &c.; and that the quantity of these substances is by no means small may be inferred from Travale's researches, from which it appears that four suffioni yielded within twenty-four hours 5000 kilos. of saline matter, consisting of 150 kilos. of boracic acid, 1500 kilos. of sulphate of ammonia, 1750 kilos. of sulphate of magnesia, 750 kilos. of the protosulphates of iron and manganese, &c. The ammonia is probably due to the decomposition of nitrogenous organic matter, occurring largely in the Tuscan mountains, the soil near the lagoons being impregnated with sulphate of ammonia. In combination with the sulphates of soda, magnesia, and iron, sulphate of ammonia forms the mineral Boussingaultite, discovered by Bechi.

3. The ammoniacal salts due to volcanic action are of no or of little value to industry. Mascagnin, sulphate of ammonia, is met with on Vesuvius and Etna; sal-ammoniac is sometimes also found on Etna, as in the years 1635 and 1669, in such large quantities as to become temporarily an article of commerce at Catania and Messina.

4. Ammonia is formed during many inorganic chemical operations, but rarely in quantities rendering its preparation or recovery commercially available. Ammonia is, for instance, set free in the preparation of caustic soda (see page 189), and the purification of caustic soda by means of nitrate of soda; the quantity of ammonia set free in this case is so large that it would be commercially worth trying to condense the gas in a coke scrubber or condenser. When arseniate of soda is prepared by dissolving arsenious acid in a caustic soda solution, evaporating this liquid to dryness, and igniting the residue with nitrate of soda, ammonia is disengaged in large quantity.

5. Under the heading "Ammonia as a by-product of the manufacture of sulphuric acid," there is in the original German text a description of a mere suggestion, embodied in a provisional specification of an English patent, for the utilisation of the waste nitrous vapours of sulphuric acid manufacture in the preparation of ammonia, by passing these vapours, with steam, through red-hot tubes or retorts filled with charcoal, the ammonia thus formed being absorbed by sulphuric acid. This process could never be available but in badly arranged sulphuric acid works, because in well managed works the escape of nitrous fumes is so very small that it certainly would not pay to convert them into ammonia.

6. Of the many unsuccessful attempts made to directly convert the nitrogen of the atmosphere into ammonia, it will only be necessary to mention Fleck's suggestion, to pass a mixture of nitrogen, oxide of carbon, and steam over red-hot hydrate of lime, whereby ammonia and carbonic acid are formed:—

$$\left.\begin{array}{l}\text{Nitrogen, } 2N\\ \text{Oxide of carbon, } 3CO\\ \text{Water, } 3H_2O\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Ammonia, } 2NH_3\text{, and}\\ \text{Carbonic acid, } 3CO_2.\end{array}\right.$$

7. Perhaps the indirect application of atmospheric nitrogen for the preparation of ammonia is of more importance. Margueritte suggests that cyanide of barium should be prepared, and its nitrogen converted into ammonia by the aid of a current of superheated steam at 300°. According to the description of this process in an English patent, not however in practice, native carbonate of baryta is calcined with some 30 per cent. of coal-tar, for the purpose of rendering the mass porous as well as more readily converted into caustic baryta at a lower temperature. The carbonaceous mass is, after cooling, placed in a retort, and kept at a temperature of 300°, while air and aqueous vapour are forced in, the result being the formation of ammonia in considerable quantity, and carbonate of baryta, which is again used. Ammonia is evolved from ball soda while cooling, during the formation of cyanogen and cyanide of potassium in blast furnaces, and the formation of sal-ammoniac in the process of iron smelting.

Organic Sources of Ammonia. Industrially speaking, the organic sources of ammonia are far more important than the inorganic. Among the ammonia-yielding organic substances coal (8) takes the first place; the average quantity of nitrogen—0·75 per cent.—contained in coal is converted into ammonia during three different processes employing this valuable mineral, viz.:—

a. By the dry distillation of coals for the manufacture of illuminating gas, ammonia is obtained in the so-called gas-, or ammoniacal gas-water, the liquid mainly consisting of an aqueous solution of sesquicarbonate of ammonia. The importance of this source of ammonia production may be inferred from the fact that the one million tons of coals yearly carbonized by the London gas-works will yield, supposing all the nitrogen to be converted into sal-ammoniac, 9723 tons of that salt.

β. Ammonia is also formed when coal is converted into coke in coke ovens. Very recently the utilisation of this source of ammonia has been successfully carried on at the large coking establishment at Alais, Département du Gard, France, and also at the coke ovens belonging to the *Société de Carbonisation de la Loire*, near St. Etienne, where, in ovens constructed according to Knab's method, large quantities of ammoniacal salts are produced.

γ. Ammonia is produced during the combustion of coal as fuel, a portion of the nitrogen contained in the coals being eliminated as ammonia; but this, it should be borne in mind, is a consequence of imperfect combustion, and consequently of loss of fuel; and although a series of experiments have been made, and apparatus devised for collecting and condensing the ammonia evolved with the smoke, the industrial production from this source has hitherto been very limited.

Ammonia from Gas-Water.

This is the most important source of ammonia production. By the dry distillation of coals for the purpose of gas manufacture there are formed, in addition to permanent gases, various vapours, some of which on cooling yield tar and ammoniacal liquor, consisting chiefly, as before stated, of a solution of sesqui-carbonate of ammonia, but containing sulphuret and cyanide of ammonium, sulpho-cyanide of ammonium, and sal-ammoniac, and being coloured by tarry matter.

It is obvious that the quantity of ammonia contained in this liquor is not always constant, but depends upon several conditions; for instance, the quantity of nitrogen contained in the gas coals, the hygroscopic moisture of the coals, and the degree of heat applied to the retorts. The nearer the retorts are kept to a bright orange-red heat, and the longer the distillation is continued, the larger the quantity of ammonia formed; for at a lower temperature, of course always above red heat, there may be formed aniline, chinoline, lepidine, and cyanogen compounds. Taking the average quantity of the hygroscopic moisture of coals at 5 per cent., and the nitrogen at an average of 0·75 per cent., 100 kilos. of coal would yield, under the most favourable conditions, 0·91 kilo. of ammonia. According to Dr. A. W. Hofmann's report (1863), coal yields, when distilled, only one-third of its nitrogen, two-thirds being retained in the coke; but no accurate experiments have been made on this subject. It has been practically ascertained on the large scale, that 1 cubic metre (=220·096 gallons) of gas-water yields at least 50 kilos. of dry sulphate of ammonia. The ammonia of the gas-water may be utilised in various ways. Where fuel is cheap, and crude sulphate of ammonia or crude sal-ammoniac marketable article, the gas-water may be at once neutralised by an acid, and the liquid thus obtained evaporated. This is done in a sal-ammoniac factory at Liverpool, where, during the colder season of the year, 300 cwts. weekly of this salt are prepared. Generally, however, the gas-water is submitted to a process of distillation, and the ammonia evolved converted into sulphate, as in Mallet's apparatus, or into sal-ammoniac, as in Rose's apparatus.

Mallet's Apparatus.

This apparatus, in use in many of the large gas-works, is shown in vertical section in Fig. 111. The plan of action is to force steam into large vessels filled with gas-water, the effect being the volatilisation of the carbonate of ammonia. Sometimes lime is added. The volatilised ammonia—of course if lime is added caustic ammonia is evolved—is next conveyed into an acid liquor, and thus converted into sulphate of ammonia. The apparatus consists of two cylindrical boiler-plate vessels, A and B. A is heated directly by the fire, and is provided with a leaden tube, *c*, dipping into the liquid contained in B, this vessel being placed to catch the waste heat from the fire. *b* and *e* are man-holes; *a* and *a′* stirrers. By means of the tube *d* the fluid from B can be run off into A. Gas-water is poured into both vessels and lime added; ammonia is set free, while carbonate of lime and sulphuret of calcium are formed, and of course remain in the vessels after the volatilisation of the ammonia. The vessel D is also filled with ammoniacal water, and when the operation is in progress this water, already warmed, is run by the aid of the tube *h* from D into B. E is a gas-water tank, from which D is filled by means of *g*. The ammonia set free in A is, with the steam, conveyed by the pipe *c* into B, thence through *c*′, into the wash-vessel, C, and thence again through *c*″, into the first condenser, D. The partially condensed vapour now passes into the condensing vessel, F, the worm of which is surrounded by cold water. The dilute ammonia is collected in G, and forced by means of the pump R into C, whence it is occasionally syphoned into either A or B. The non-condensed ammoniacal gas is carried from G, through a series of Woulfe's bottles, the first bottle, H, containing olive oil for the

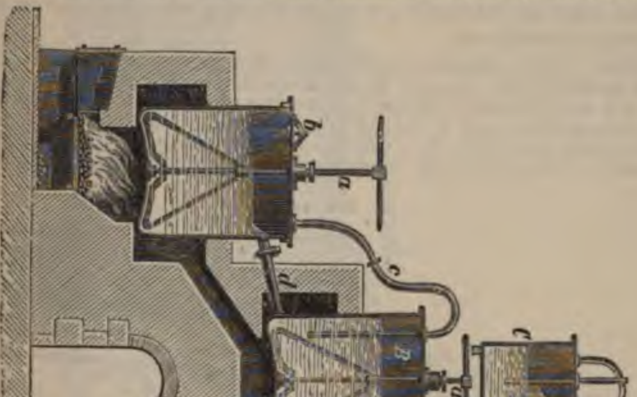
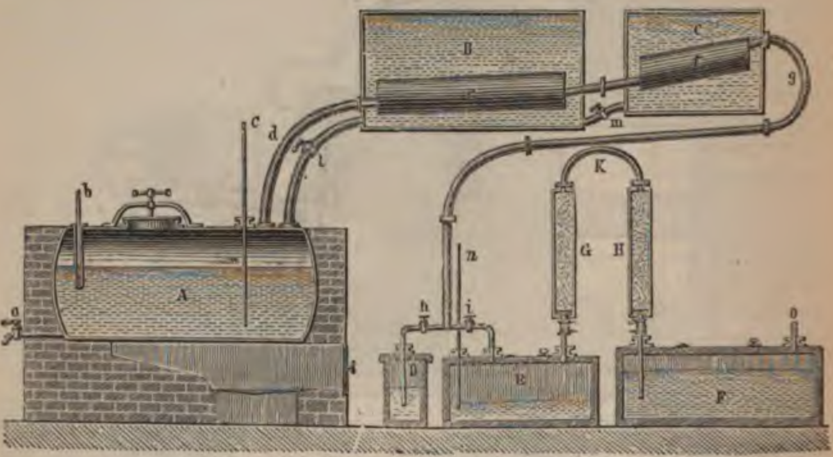


Fig. 111

purpose of absorbing any hydrocarbons mixed with the gas; the bottle I contains caustic soda ley, in order to purify the ammonia and retain impurities; the bottle K is half-filled with distilled water. The ammoniacal gas having passed through K, is conveyed to the large lead-lined wooden tank, L, filled with dilute sulphuric acid if it is intended to prepare sulphate of ammonia, or with water for making liquid ammonia. The vessel L is placed in a tank of water; *i* is a small pipe for introducing acid; while the tube leading to M serves to carry off any unabsorbed ammonia, M being also filled with acid.

Rose's Apparatus. In the manufacture of liquid ammonia the apparatus devised by Mr. Rose, and shown in Fig. 112, may be advantageously employed. It consists of:—A, a boiler; B and C, two vessels in which the gas-water is warmed by the aid of the tubes, *e* and *f*, through which and *g* the steam and ammonia gas evolved in A pass to the absorption vessels, D, E, and F, the connection between E and F being formed by the gas-filters, G and H. The ammoniacal water can be run into A by means of the tubes, *l* and *m*, each of which is fitted with a tap or stopcock. A is filled two-thirds with gas-water and one-third with slaked lime. The cylindrical sheet-iron gas-filters, G and H, are filled with freshly burnt charcoal to retain any empyreumatical matter which might be carried over by the gas. The absorption vessel, D, is filled with hydrochloric acid, while pure water is poured into E and F. When A is filled, and the rest of the apparatus put in working order, the fire is kindled, the ammoniacal gas evolved in A passes with the steam to B and C, where a portion of the steam is condensed and retained as water in *e* and *f*. Into the boiler, A, is fitted a tube, *b*, containing a thermometer, surrounded by brass fittings for the better conduction of the heat; when this thermometer indicates 92° to 94°, the tap *h* is opened, and the tap, *i*, open up to this time, shut in order to cause the gas to pass into the hydrochloric acid contained in D, until the vessels G and H have been filled with fresh charcoal, an operation which is required at the beginning of the working as well as when the temperature in A has risen to 96°, 98°, and 100°. This having been done, the tap *h* is again opened. When the temperature has reached 103°, taking the boiling-point of the liquid at 100°, all the ammonia is expelled, and the liquid is then run off by opening the stopcock, *a*. Fresh lime having been put into the boiler, the operation is repeated. When the temperature in A reaches 103°, the liquid in B becomes heated to 90°, and that in C to from 25° to 30°. The vessel F contains from 120 to 150 litres of water, which is converted into liquid ammonia of a sp. gr. = 0·910 to 0·920. *c* and *n* are glass safety tubes.

FIG. 112.



Lunge's Apparatus. This apparatus, also intended for the utilisation of gas-water, is shown in Fig. 113; *a* is the boiler; *h* the gas tube connected with the worm, *c*, which is placed in a tank, *d*, filled with gas-liquor, run into *a* by means of the tube *e*. The tube *f* is so fitted to *a* as to admit of discharging the waste liquor readily. *b* represents a stirrer fitted to the boiler by a stuffing box, and being intended to rake up the lime and prevent it getting caked to the bottom of *a*; *h* 1, a tube intended for running gas liquor into *d*, from a tank placed at a higher level; *i*, a tube provided with a tap and fitted to the cover of *d*, to

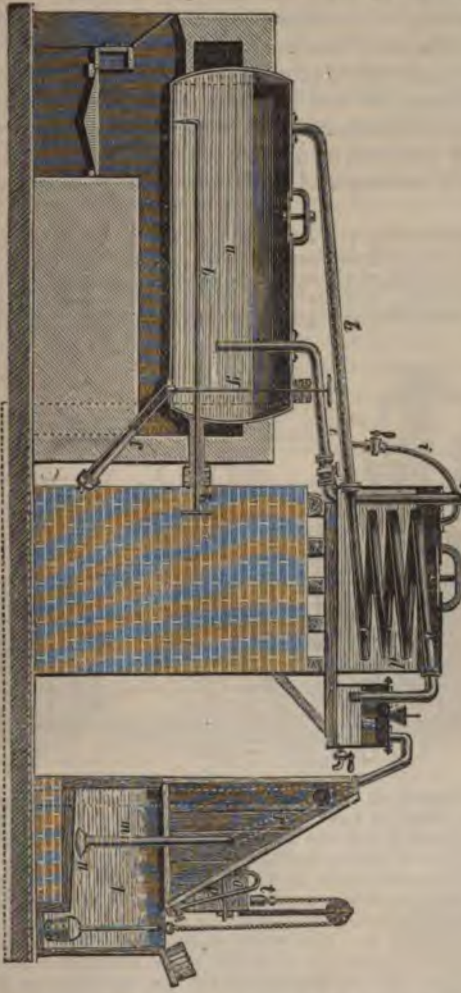


FIG. 113.

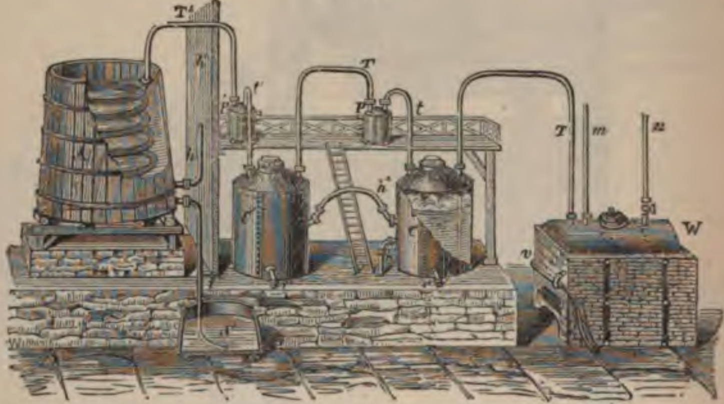
convey any gas or vapours from *d* into the worm. *k* represents a wash vessel, sometimes filled simply with water, at others with milk of lime. The gas and vapours having passed through *k*, are conveyed to the absorption vessel, *l*. The tube, *m*, through which the gas passes, is funnel-shaped, and opposite to the mouth of the funnel, at the bottom of the tank, a thick disc of lead is fixed, because at this spot the action of the gas would soon wear away the leaden lining of the vessel. *o* is a smaller wooden tank, also lead-lined, into which sulphuric acid is poured, and whence it runs into *l* through the stoneware syphon, *p*. Any vapours given off are caught by the hood, *r*, and thence conveyed by a tube into the chimney. The saline matter deposited in *l* is removed by a leaden pail, as shown in the cut; when this pail is filled it is drawn up by means of the chain and pulley aided by the counter weight, *t*. The salt (sulphate of ammonia) is placed in the basket, *u*, from which the mother-liquor adhering to the salt drains again into the tank, *l* Evaporation is therefore unnecessary with this apparatus.

Ammonia from Lant.

9. Lant, or stale urine, is a very important source of ammonia. Whenever nitrogenous organic bodies are decaying, ammonia is always formed; when the organic substance is a proteine compound, there is formed carbonate of ammonia as well as sulphuret of ammonium; but when the organic substance contains no sulphur, only carbonate of ammonia is formed, as is the case with the urea, CH_4N_2O, contained in urine, the urea by taking up the elements of the water being converted into carbonate of ammonia. Lant is frequently employed without further preparation for various purposes, on account of the carbonate of ammonia it contains, as, for instance, in washing wool and removing the fat from flannel and other woollen fabrics.

The apparatus exhibited in Fig. 114, contrived by Figuera, and until lately in operation at a large establishment for the utilisation of the contents of the latrines and cloacæ of Paris, consists of a steam-boiler, W, the steam generated in which is conveyed to two large iron cylinders filled with lant. The carbonate of ammonia expelled is, with the steam, condensed in a leaden worm; the cooled liquid is conveyed to a tank filled with acid, and thus converted into carbonate of ammonia. The arrangement of the apparatus is as follows:—The wooden vessel, A, contains some 250 hectolitres of lant, and is filled by means of the tube *h*. C and C′ are two cylindrical sheet-iron vessels of 100 hectolitres capacity; P and P′ are similar vessels, the use of which will be presently explained. At the commencement of the operation the boiler, W, is filled with about 130 hectolitres of exhausted lant, taken from the vessels C and C′. The lant in A, warm in consequence of having served for condensation, is conveyed to C by a tube, and thence by the tube *h″* to C′, cold lant being poured into A. The boiler, W, is fitted with three tubes, viz., T, the steam pipe, *m*, a safety tube, brought to within a few centimetres from the bottom of the boiler, and carried above the roof of the shed, and *n* a smaller safety tube; V is a tube fitted with a stopcock. The steam evolved in W is carried by T into C′, evolving from the liquid therein the carbonate of ammonia it holds in solution. The carbonate, with the steam passes through *t* into the vessel, P, which serves to retain any liquid carried over from C′. The carbonate of ammonia vapour now passes from P through the tube T′ to C, and taking up in that vessel more carbonate of ammonia, is conveyed through the tube T′ into P′ (which again serves the purpose of P), and thence through T″ into the leaden worm of the condensing apparatus. The condensed liquor, a more or less concentrated solution of carbonate of ammonia, is run through *t″* into S, a wooden vessel, lead lined, and filled with a sufficient quantity of sulphuric acid to saturate the carbonate of ammonia. The whole operation lasts about twelve hours; after this time the waste liquid in the boiler is run off by opening the stopcock, V, and the operation again repeated. On an average the lant operated upon at Bondy, near Paris, yields per cubic metre from 9 to 12 kilos. of

FIG. 114.



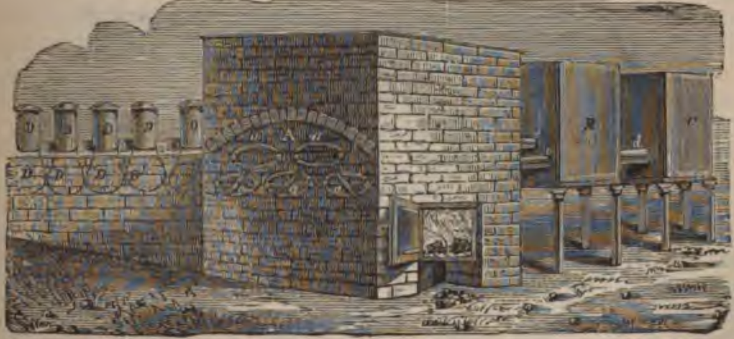
sulphate of ammonia, and at each operation 200 kilos. of that salt are obtained by the working of one of the apparatus just described. It is stated that from the 800,000 cubic metres of urine yearly run waste in Paris alone, there could be obtained, by proper treatment, 7 to 800,000 kilos. of sulphate of ammonia.

Ammonia from Bone. 10. By the destructive distillation of animal substances, such as bones, hoofs of horses, refuse horn, skins, hides, decayed meat, &c., there is obtained a series of products, among which carbonate of ammonia prevails, with cyanogen compounds, sulphuret of ammonium, and tarry matter—a very complex liquid containing pyrrol, bases of the ethylamin series, pyridin, C_5H_5N, picolin, C_6H_7N, lutidin, C_7H_9N, and collidin, $C_8H_{11}N$. The organic matter of these substances contains from 12 to 18 per cent. nitrogen; the organic matter of bones contains 18 per cent. of nitrogen, and, as the organic matter amounts to about one-third of the weight of the bones, these contain about 6 per cent of nitrogen. Buffalo horn contains 17, waste woollen fabrics 10, and old leather 6·7 per cent. of nitrogen.

It is evident that the quantity of ammonia in the products of the dry distillation of animal substances depends upon the kind and condition of these materials, and upon the temperature at which the operation takes place. The carbonate of ammonia is obtained in the condensers as a solid saline mass, the crude *sal cornu cervi*, or in aqueous solution (so called *spiritus cornu cervi*), floating on the surface of the tar. At the present time the manufacture of ammonia and its salts from the products of the dry distillation of animal substances is a matter of but limited industrial importance, owing to the extended coal-gas manufacture. Indeed, dry distillation is now only carried on for the purpose of obtaining animal charcoal, and the occurrence of ammoniacal products is rather considered as a necessary but unavoidable evil. A large quantity of animal matter is used for the manufacture of phosphorus and of prussiates, and in these operations the manufacture of ammoniacal salts is either altogether out of the question or effected only on a limited scale.

The apparatus used for the destructive distillation of animal matter is in some respects similar to a coal-gas oven. Fig. 115 exhibits the construction in general use for what is termed animal charcoal burning. The retorts intended to contain the bones are set in furnaces and fitted at the end farthest from the mouth with tubes, *c c*, communicating with leaden chambers, B, C, &c. In these chambers the vapours are condensed, forming a solid saline mass, which is purified by sublimation in the iron vessels, D D, fitted with leaden covers. If, instead of bones, other animal matters, for instance, horn, woollen rags, hair, and leather-cuttings, are operated upon, the result is that, instead of solid

FIG. 115



carbonate of ammonia, an ammoniacal fluid of 13° to 15° B. is obtained, which may be utilised in various ways. Where the mother-liquors of salt-works are readily obtainable, they may, especially if rich in chloride of magnesium, be employed for the preparation of sal-ammoniac by using the hartshorn spirit (crude carbonate of ammonia solution) for the precipitation of the chloride of magnesium solution.

Ammonia as a By-Product of Beet-Root Sugar Manufacture.

When the beet-root juice is boiled, ammonia is evolved in large quantities, and may be utilised in the preparation o sulphate of ammonia. The ammonia yielded by the juice is the product of the decomposition of the aspartic acid and betain present in the roots. According to Renard, a beet-root sugar manufactory which yearly consumes 200,000 cwts. of beets might thus obtain 887 cwts. of sulphate of ammonia.

Technically Important Ammoniacal Salts.

Sal-ammoniac, chloride of ammonium, NH_4Cl, consists in 100 parts of—

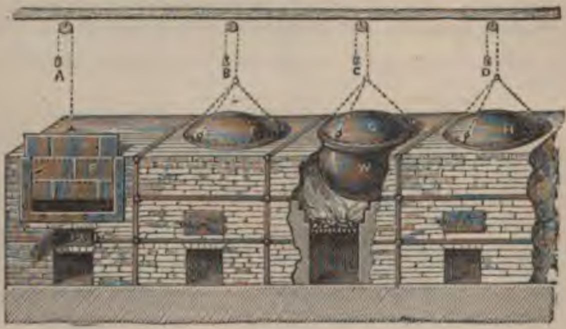
Ammonia,	31·83	or	Ammonium,	33·75
Hydrochloric acid,	68·22		Chlorine,	66·25

From the thirteenth to the middle of the eighteenth century this salt was imported into Europe exclusively from Egypt, where it was obtained by the combustion of camel's dung. The camel feeds almost exclusively upon plants containing salts, and the sal-ammoniac is sometimes found ready formed in the animal's stomach. The sal-ammoniac having sublimed with the soot from the combustion of the dung, was collected and refined by a second sublimation.

In localities where dung is used as fuel, it has been tried to obtain sal-ammoniac by combustion with common salt. The first sal-ammoniac manufactory in Germany was established by Gravenhorst Brothers, at Brunswick, in 1759. We have already seen how crude sal-ammoniac may be prepared from gas-water or by other means.

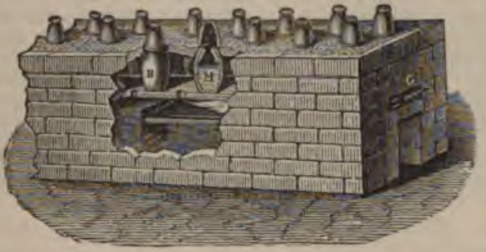
The salt, no matter whence derived, is purified by sublimation in cast-iron cauldrons, W, Fig. 116, lined with fire-clay. As soon as the crude sal-ammoniac is put into these vessels and tightly rammed, heat is applied, at first gently, so as to drive off any moisture. This effected, iron lids, F, G, H, are luted to the cauldrons; the lids can be readily moved by means of the pulleys and chains provided with counterweights, B, C, D. Instead of iron covers lead hoods sometimes are employed, the opening of which is temporarily closed with an iron disc. The hoods or covers are always securely fastened to the cauldrons, to prevent them being forced off by the pressure of the vapours. The temperature has to be regulated during the process with great nicety, for too low a degree of heat yields a loose salt, and with too high

FIG. 116.



a degree of heat the organic matter present in the crude sal-ammoniac is liable to give off empyreumatic matter, spoiling the appearance of the sublimed salt and interfering with its good quality. Experience has proved that it is expedient to have the sublimation vessels of rather large size, 2½ to 3 metres interior diameter. When the sublimed sal-ammoniac cake has attained a thickness of 6 to 12 centims. the operation is discontinued, and the cake removed. The furnace is provided with an oven for drying the sal-ammoniac, this oven being shut with a door, E, movable by means of a chain running over a pulley, and aided by a counterpoise. At the present day sal-ammoniac is often sublimed in earthenware vessels or large glass flasks, the crude salt being first mixed with 20 to 30 per cent. of its weight of powdered animal charcoal, then dried over a good fire, and next put into the stoneware sublimation vessels, B and M, Fig. 117, placed in two rows over the fire-place, G.

Fig. 117.



Each of these vessels is 50 centims. in height; the openings are surrounded by an iron plate properly fitted to the neck and provided with a flange upon which rest the earthenware vessels wherein the sublimed sal-ammoniac is condensed. When glass flasks are used, the height of these vessels is 60 centims. by 30 centims. diameter. Sixteen of these flasks, each charged with 9 kilos. of the mixture of sal-ammoniac and charcoal, are placed upon a furnace in cast-iron pots, which are filled with sand. The cover is in this case a leaden plate. The sublimation is carefully conducted, and goes on slowly, lasting about 12 to 16 hours. After this time, the leaden plates are removed, bungs or plugs of cotton-wool inserted, and the flasks allowed to cool very gradually, for as the salt expands on cooling the glass vessels may be broken. The cake of sal-ammoniac when quite cool is scraped clean with a knife, and afterwards presents a perfectly crystalline appearance. When it is desired to obtain the salt free from iron, the crude salt should be mixed, before the sublimation, with about 5 per cent. of superphosphate of lime, or with 3 per cent. of phosphate of ammonia; by this addition any chloride of iron is decomposed and left in the retort as phosphate. The sal-ammoniac of commerce is met with either in crystalline state or as a compact fibrous sublimed material; in the latter case the cakes or discs have a meniscus shape, weigh abroad from 5 to 10, but in England usually about 50 kilos., and exhibit the appearance of having been formed in layers. Crystalline sal-ammoniac is obtained by adding to previously re-cystallised sal-ammoniac a boiling hot and saturated solution of the same salt, so as to form a thickish magma, which is next placed in moulds similar in shape to those in use for making loaf-sugar; after draining, the loaf of sal-ammoniac is removed, dried, and packed in paper ready for sale. Besides the use made of sal-ammoniac in chemical laboratories, by pharmaceutists and veterinary surgeons, it is industrially in demand for tinning, zincing, and soldering, in calico-printing and dyeing, in the manufacture of paints and pigments, in the preparation of platinum, snuff, and very largely in the preparation of a mastic—1 part of sal-ammoniac, 2 of sulphur, and 50 of iron-filings—used in joining steam-pipes, the sockets and spigots of iron gas- and water-pipes, &c. Sal-ammoniac is also employed in the preparation of pure *ammonia liquida* and ammoniacal salts.

Sulphate of Ammonia. It has been already mentioned that sulphate of ammonia—

$$(NH_4)_2SO_4,$$

is met with native in small quantities in the mineral known as mascagnin, in larger quantities in the boracic acid of Tuscany, while it is also found in Boussingaultite.

The modes of preparing this salt from the ammoniacal water of gas-works, lant, the products of the dry distillation of bones, by the aid of sulphuric acid, or by double decomposition by means of gypsum or sulphate of iron, have been already given. The concentration of the weak solution by evaporation yields the crystalline salt, which, however, when obtained from liquors containing tarry matters is usually of a deep brown colour, and has therefore to be purified by being dissolved in hot water, filtered through animal charcoal, and then re-crystallised, the best plan being to evaporate the solution rapidly, and remove the salt gradually by means of perforated ladles. The salt is then drained by being placed in baskets, and next quickly dried on heated fire-clay slabs, in which operation any particles of tar are decomposed. Sulphite of ammonia obtained by saturating carbonate of ammonia solution with sulphurous acid gas is, when exposed to air, gradually converted into sulphate. Sulphate of ammonia is, industrially speaking, far the most important of the ammonia salts, because besides being very largely used in artificial manure mixtures, and by itself for the same purpose, it is extensively employed in alum-making, and is the starting-point of the preparation of chloride of ammonium, carbonate of ammonia, liquid ammonia, and other similar products.

Carbonate of Ammonia. The salt used in pharmacy and industry under this name is in reality sesquicarbonate of ammonia, and composed according to the formula

$$(NH_4)_4C_3O_8, \text{ or } 2\,([NH_4]_2CO_3) + CO_2.$$

It is obtained either directly from the products of the distillation of bones, or by subliming a mixture of chalk and sal-ammoniac.

Among the products of the dry distillation of bones is found a solid sublimate, essentially impure carbonate of ammonia, purified by sublimation. For pharmaceutical use carbonate of ammonia is prepared by submitting a mixture of either chloride of ammonium or sulphate of ammonia with chalk—4 parts of the ammonia salt, 4 of chalk, and 1 of charcoal powder—to a low red heat. The product is a perfectly pure white salt; during the operation a large quantity of ammoniacal gas is evolved, which is either absorbed by water or by coke moistened with sulphuric acid. Kunheim decomposes the sal-ammoniac by subliming it with carbonate of baryta, chloride of barium being obtained as a by-product. When freshly prepared, carbonate of ammonia is a transparent crystalline mass, which, while absorbing water from the atmosphere, and evolving ammonia, is superficially converted into bicarbonate of ammonia (hydrocarbonate of ammonia, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}CO_3$). Owing to the penetrating odour emitted by this salt, it is known as smelling salts. Impure carbonate of ammonia is also used for cleaning woollen and other fabrics, for the removal of grease from cloth, and further, for the extraction of the orchil pigments. Pure carbonate of ammonia, besides its use in pharmacy, is an ingredient of baking and yeast powders.

Nitrate of Ammonia. This salt, $(NH_4)NO_3$, is prepared by the double decomposition of solutions of sulphate of ammonia and nitrate of potassa. The sulphate of potassa is first separated, and the solution of ammonia nitrate having been concentrated by evaporation is left to crystallise, its crystalline form being similar to that of saltpetre. When dissolved in water this salt produces cold, and is therefore used in freezing mixtures; while the fact that when strongly heated it is converted into protoxide of nitrogen and steam ($N_2O + 2H_2O$) might perhaps render it of use in the preparation of a blasting powder.

SOAP-MAKING.

Soap. By soap we understand the product of the action of caustic alkalies upon neutral fats, and consequently soap may to all purposes be considered to consist of stearate, palmitate, and oleate of potassium or sodium. Although soap has been manufactured from a very remote antiquity, this industry did not attain its present development upon scientific and rational principles until Chevreul published the results of his researches on the fats, and before the discovery of Leblanc called the soda industry into existence.

Raw Materials of Soap-boiling. The raw materials used in soap-boiling, as soap manufacture is usually termed in this country, are of two kinds, viz., fatty substances and solutions of caustic alkalies. Among the more important fatty substances are the following:—Palm-oil, of vegetable origin, met with in the fruit of a palm tree, *Avoira elais* or *Elais guianensis;* according to others, however, this oil is derived from the *Cocos butyracea*, *C. nucifera*, and *Areca oleracea*, trees growing wild, and also cultivated in Guinea and Guiana. The colour of this oil is a red-yellow, its consistency that of butter, while it possesses a strong but by no means disagreeable odour, similiar somewhat to that of orris root. When fresh, this oil melts at 27°, but by becoming rancid as it is termed—that is, by its decomposition into glycerine and free fatty acids—its melting point rises to 31° and even to 36°. It is chiefly composed of palmitine mixed with a small quantity of oleine. Palmitine, formerly confused with margarin, is saponified by the alkalies and converted into palmitate of potassa or soda, while glycerine is set free:—

$$\left.\begin{array}{l}\text{Palmitine (tripalmitine), } \left.\begin{matrix}C_3H_5,\\(C_{16}H_{31}O)_3\end{matrix}\right\}O_3\\ \text{Hydroxide of potassa, } 3KOK\\ \quad\text{(caustic potassa)}\end{array}\right\} = \left\{\begin{array}{l}\text{Glycerine, } \left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3,\\ \text{Palmitate of potassa, } 3\left\{\begin{matrix}C_{16}H_{31}O\\K\end{matrix}\right\}O.\end{array}\right.$$

Palmitic acid is very similar to, and has often been confused with, stearic acid; the former is in a pure state a solid white crystalline mass, which fuses at 62°. Palm-oil often contains one-third of its weight of this acid in free state, and the quantity increases with the age of the oil. The red-yellow pigment of the palm-oil not being destroyed by its saponification, the soap made from this oil is of yellow colour, but if, previous to saponification, the oil is submitted to a bleaching process, that is to say, the pigment destroyed by chemical agents, such as the joint action of bichromate of potassa and sulphuric acid, the oil becomes nearly white, and yields, on being saponified, a white soap.

The illipe, or bassia-oil, very similar to palm-oil, is obtained by pressure from the seeds of the *Bassia latifolia*, a tree growing on the slopes of the Himalaya. At first the colour of this oil is yellow, but by exposure to sunlight it becomes white. Its odour is not very strong, but rather pleasant. At the ordinary temperature of the air this oil has the consistency of butter; its sp. gr. is = 0·958; its melting-point 27° to 30°. It is somewhat soluble in alcohol, readily in ether, and easily saponified by potassa and soda. In its saponification, oleic acid and two solid acids with a variable melting-point are formed. The galam butter produced by the *Bassia butyracea*, a tree met with in the interior of Africa, is sometimes confounded with palm-oil, to which it is very similar, but of a deeper red colour. Galam butter fuses at 20° to 21°, and is in its properties very much like palm-oil. Carapa oil and vateria tallow belong to the same class of fatty substances; the first, the product of the kernel of a species of *Persoonia*, a palm tree met with in Bengal and Coromandel, is a bright yellow coloured material, which at 18° separates into an oil and a solid fat; known as pine-tallow, Malabar tallow, and obtained from the fruits of the *Vateria indica*, is a white-yellow waxlike-tallow, melting at 35°. Mafurra tallow is obtained by boiling in water the seeds or kernels of the mafurra tree found at Mozambique; this seed, very rarely seen in Europe, is of the size of small cacao beans. Mafurra seed also occurs in the Islands of Madagascar and Isle de Réunion. The fat obtained from this seed has a yellow colour, the smell of cacao butter, and melts more readily than tallow. The fat of the seeds of the *Brindonia indica*, employed at Goa, instead of butter, also for medicinal purposes, and for use in lamps, is nearly white; melts at 40°, and is insoluble in cold, but somewhat soluble in boiling alcohol. Cocoa-nut oil, obtained from the kernels of the cocoa-nut (*Cocos nucifera*, *C. butyracea*), is largely used in the tropics, where the tree abounds. This oil is imported into Europe, and is also obtained here by pressing and by treating the kernels of the imported nuts with sulphide of carbon. It is white, has the consistency of lard, but possesses a disagreeable odour and a somewhat foliated texture; its melting-point is 22°. Chemically considered this fat consists of a peculiar substance termed cocinin, with small quantities of oleine; by saponification the former yields glycerine and cocinic acid (cocoa-stearic acid), $C_{13}H_{26}O_2$. W. Wicke obtained in 1860, 61·57 per cent. of fat from the kernels. During the last twenty years cocoa-nut oil has been largely used for soap-boiling, because it is an excellent material for the preparation of so-called fulling soaps. Tallow is obtained by melting the fatty matter deposited in the cellular tissue of the abdominal cavity of cattle and sheep. The hardness of the tallow depends partly upon the animals from which it is derived, partly upon the food they eat; if the food be fodder, the hardest tallow is produced, while if it consists of the refuse from breweries and distilleries the tallow is soft. Russian tallow owes its hardness to the fact that the cattle in that country are for fully eight months in the year kept on dry fodder. Generally tallow melts at 37°, and contains 75 per cent. of its weight of solid fatty matter, stearin (tristearin) and palmitin (tripalmitin), the remainder being olein. If previous to being melted—that is, separated by the application of heat from the cellular tissue and membranes in which it is enclosed—tallow is preserved for too long a time, it obtains a bad odour, removed with difficulty. The operation known as tallow-melting can be performed in two ways, either by simply applying heat, which causes the cellular tissue to shrink and become dry, the fat being expelled; or the membranes and cellular tissue are destroyed by chemical agents, viz., the use of either sulphuric or nitric acid, or caustic ley. Among these methods, that of D'Arcet, in which sulphuric acid is used, and the operation carried on in closed vessels, is one of the best; the sulphuric acid decomposes the vapours which are given off and destroys their fœtidity, while more tallow and of a better quality is obtained. The vapours are carried either into the furnace or into condensing apparatus. D'Arcet recommends that to 100 parts of cut-up tallow, 1 part of sulphuric acid and 50 parts of water should be used. While the loss by the ordinary method of tallow-melting amounts to 15 per cent., it is only 5 to 8 per cent. when this method is employed.

Lard, owing to its high price, is rarely used in Europe for making soap, but is largely employed in the United States, where, especially at Cincinnati, enormous quantities of lard are converted into a solid fat (42 to 44 per cent.), and into a fluid oil (lard oil, 56 to 58 per cent.)

Olive-oil is obtained from the fruit of the olive tree, *Olea Europea*, belonging to the natural order of the *Jasmineæ*, and largely cultivated in the whole of Southern Europe and the coastlands of North Africa.

In order to obtain an oil of good quality it is essential that the olives should be gathered when they are fully ripe, which happens in the months of November and December. Unripe olives yield an oil having a harsh bitter taste, while, again, over-ripe fruit yields a thick oil, readily becoming rancid. The method of oil extraction from olives as carried on in Southern France is the following:—The ripe olives are first reduced to pulp in a mill; this pulp is put into sacks made of strong canvas, or, better, of horsehair, and submitted to pressure. The first portion of oil thus obtained is the best, and is known as virgin oil, or *huile vierge*. In order to eliminate all the oil as much as possible, the cake, after the first pressing, is treated with boiling water and again pressed. The oil thus obtained possesses a fine yellow colour, but is more liable to become rancid than the virgin oil. Notwithstanding the second pressure the cake retains enough oil to make it worth while to submit it to further operation. Some kinds of olive-oil obtained by the second pressing are employed, under the name of Gallipoli oil, in dyeing Turkey-red. This oil has an acid reaction, consequent upon its containing free fatty acids, is turbid, rancid, and possessed of the property of forming with carbonates of alkalies a kind of emulsion, which in dyeing is known as the white-bath. The olive-oil used for the purpose of greasing wool in spinning is known as lampant-oil. Under the name of *Huile d'enfer* is understood the olive-oil deposited in the tanks, where the water used for adding to the olives about to be pressed is kept; it is used in the manufacture of soap. During the last few years it has become the custom to exhaust the olives with sulphide of carbon instead of pressing them.

Fish-oil, seal-oil, obtained from the thick skin of several varieties of mammalia inhabiting the seas, especially of the colder regions of the globe, and belonging to the cetacea and phocena, varies somewhat in its properties, according to the mode of preparation and the animal from which it has been derived. The sp. gr. of this oil is 0·927 at 20°; when cooled to 0° it deposits solid fat; it is readily soluble in alcohol, and consists of oleine, stearine, and small quantities of the glycerides of valerianic and similar fatty acids. Fish-oil, besides being an important material in soap-making, is also used in tanning, tawing, and leather-dressing operations. Hemp-oil, obtained from the hemp-seed (*Cannabis sativa*) containing about 25 per cent. of oil, is chiefly used for making black, green, or soft soap. When fresh pressed, hemp-oil possesses a bright green colour, which in time becomes a brown-yellow. Linseed-oil, like the former a so-called drying oil, is obtained from the well-known linseed (*Linum usitatissimum*) containing about 22 per cent. of this oil, the sp. gr. of which is at $12^\circ = 0{\cdot}9395$. This oil consists chiefly of a peculiar glyceride which on being saponified yields a fatty acid different from oleic acid; moreover, linseed-oil contains some palmitin. Castor-oil, from *Ricinus communis*, behaves when saponified very much like cocoa-nut oil. As yet, however, this oil is not used in soap-making. Rapeseed-oil, as it occurs naturally, does not yield so good a soap when saponified as when the oil is first converted into *rapselaidin*, which, according to A. Müller, is done in the following manner:—To 1 cwt. of the oil is added 1 lb. of nitric acid diluted with 1½ to 2 lbs. of water; next some iron nails are added, and the acid fluid is well stirred through the oil with a wooden spatula. By the action of the nitrous acid set free, the oil is gradually converted into a yellow fatty mass, which after having been left standing for some weeks in order to solidify, may be directly saponified with soda. The oleic acid largely obtained in the manufacture of stearine candles is a very important material in soap-making. This acid is a solution of impure stearic and palmitic acids in oleic acid.

Colophonium, the residue of the distillation of oil of turpentine, a yellow or black-brown coloured material, is largely imported from the United States for the purpose of preparing resin soaps, for sizing paper, and for the preparation of yellow soaps, which are resin and tallow saponified together in certain proportions.

Ley. The other important material required for soap-making is the ley; that is to say, an aqueous solution of caustic potassa or caustic soda. Ley is not so much a constituent of soap as the material by which the chemical process termed saponification is brought about. Usually the soap-boiler prepares the caustic ley, and formerly wood-ash or potash was used for this purpose, but at present soda is more extensively employed. The conversion of the alkaline carbonates into caustic alkalies is effected by means of quick-lime; but abroad chemical manufacturers produce caustic soda, and sell it to the soap-boilers under the name of soap-stone.

The preparation of soap-boilers' ley from wood-ash is carried on in the following manner:—The sifted ash is placed on a paved floor, and moistened with enough water to render it somewhat pasty. This paste is then formed into heaps, constructed with an indentation, into which the caustic lime in quantities of one-tenth to one-twelfth of the weight of the ash is placed. Over the lime is next poured sufficient water to cause it to slake, care being taken to cover the lime up with ash. The ash and lime having been thoroughly mixed, are placed in a tank, shaped like a cone from which one-fourth of the narrow part is cut off, and fitted near the bottom with a tap. At a distance of some five inches from the bottom a false and perforated bottom is fixed, so that the ley can collect between the two bottoms. Under the tap a large iron tank is placed to receive the ley. The mixture of ash and lime having been placed upon a layer of straw upon the perforated bottom, and care having been taken to squeeze the mass together, water is poured over it for the purpose of lixiviating the material until completely exhausted. Usually three different kinds of ley are prepared and kept, viz.—1. Strong ley, 18 to 20 per cent. of alkali; 2. Middling strong ley, 8 to 10 per cent. of alkali; and 3. Weak ley, containing only 1 to 4 per cent. of alkali. This weak liquor is commonly used instead of water for lixiviating a new ash and lime mixture. The sodium-aluminate obtained by the decomposition of cryolite is used in the United States under the name of "*Natrona refined saponifier*," for soap manufacturing purposes. Sulphuret of sodium may also be used instead of caustic alkali.

Theory of Saponification. Before Chevreul published his researches, it was supposed that fats and oils possessed the property of combining with alkalies. Chevreul found, however, that fats separated from their state of combination as soaps possessed properties differing from those existing before they were saponified, the fact being that the substances we are acquainted with as oil or fats are compounds of peculiar acids, stearic, palmitic, margaric, oleic, all non-volatile substances; while certain fats which give off a peculiar odour contain in addition to these acids volatile fatty acids, as butyric, capric, capronic, valerianic, &c. The volatile acids in the ordinary oils and fats are combined with a sweet material, discovered by Scheele, and known under the name of glycerine.

According to Berthelot's researches it is held that all the oils and fats which are used in soap-making are ethers of glycerine, $C_3H_8O_3$, that substance being viewed as a trivalent alcohol, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$. Palmitin, for instance, the main constituent of palm-oil, is glycerlyl-tripalmitate, or tripalmitin, that is to say, glycerine in which three atoms of hydrogen are replaced by the radical of palmitic acid, $\left.\begin{matrix}C_3H_5\\3C_{16}H_{31}O\end{matrix}\right\}O_3$.

Stearine (tristearine) and oleine (trioleine) have an analogous constitution. When the fats, take palm-oil for instance, are saponified with caustic alkalies, say caustic soda, the fat—that is, in chemical parlance, the ether—is decomposed into alcohol, *i.e.*, glycerine, and sodium palmitate, *i.e.*, soap, according to the following equation:—

$$\left.\begin{array}{l}\text{Tripalmitin } \left\{\begin{array}{l}C_3H_5\\3C_{16}H_{31}O\end{array}\right\}O_3\\ \text{and Caustic soda, } 3NaOH,\end{array}\right\}\text{yield}\left\{\begin{array}{l}\text{Glycerine, } \left.\begin{array}{c}C_3H_5\\H_3\end{array}\right\}O_3\\ \text{and Soap, or sodium palmitate, } 3\left\{\begin{array}{l}C_{16}H_{31}O\\Na\end{array}\right\}O.\end{array}\right.$$

The glycerine formed during the process of saponification remains, after the separation of the soap, dissolved in the mother-liquor from which it is prepared. It is clear that such fats as palm- and cocoa-nut oil, which in their ordinary state contain fatty acids, are more readily saponified than the perfectly neutral fats, viz., olive-oil and tallow; while the oleic acid derived from the stearine candle manufactories is readily saponified by carbonated alkalies. This observation applies to colophonium (resin), which consists essentially of a peculiar acid, pinic acid, but in these instances no real saponification takes place, inasmuch as no glycerine is formed. The decomposition of a fat by an alkali does not take place suddenly and throughout the whole of the fat at once, in the manner of inorganic salts, but passes through several stages, the first being the formation of an emulsion of ley and fat; next fat acids and fat acid salts are formed, retaining the rest of the fatty matter in suspension; gradually the free fatty matter is saponified, and the fat acid salts are converted into neutral salts, or in other words, soap.

When caustic potassa is used, soft soaps are produced, while the hard soaps result from the use of caustic soda. We distinguish soaps:—

a. As hard soaps or soda soaps.
β. As soft soaps or potassa soaps.

According to the fatty substances used in soap-boiling, soaps are distinguished as tallow, oil, palm-oil, oleic acid, cocoa-nut, fish-oil, and resin soaps, &c. Technically, hard soaps may be divided into:—

1. Nucleus soaps.
2. Smooth soaps.
3. Fulling soaps.

The term nucleus soap designates the soap that after having been made and separated from the ley by the aid of common salt is boiled down to a uniform mass, free from air bubbles, and exhibiting after solidification small crystalline particles. The portion of the soap which does not separate in that state assumes, by becoming mixed with a large or smaller quantity of the impurities of the ley, a mottled appearance. The soap directly separating by the addition of salt into globules or nuclei is pure soap, free from any adhering ley, water, or glycerine. Smooth soap is obtained by boiling for some time with either water or weak ley, the soap taking up a portion of the water, and losing the crystalline and mottled appearance. In the preparation of this soap it is first separated by means of salt from the mother-liquor (in saline solutions soap is insoluble), but after that separation the soap is boiled with weak ley. The only difference existing between the two kinds is, that the latter contains more water than the former. The fulling soap, at the present that chiefly met with in commerce, is essentially the worst kind of soap, as an insufficient quantity of salt is used, the result being that the entire contents of the boiling-pan are kept together. The process of boiling is continued until on cooling the mass solidifies. The soap is removed, cut into bars, and sold. Soap made from cocoa-nut oil possesses especially the property of being hard and dry, notwithstanding that it contains a large amount of water; consequently the use of cocoa-nut oil, both alone and with other fats to which it imparts its property, is greatly on the increase. Soaps of this kind will produce 250 to 300 parts of soap from 100 of oil.

Chief Varieties of Soap.

The German tallow soap or curd soap is essentially a mixture of stearate of soda and palmitate of soda, and is commonly prepared indirectly by first saponifying tallow with caustic potassa, and next converting, by means of common salt, the stearate and palmitate of potassa into the corresponding soda compound.

substances. Soap of this kind (in Germany known as Eschweger soap) appears when freshly made quite hard and dry, though containing such a large quantity of water. It is possible to make from 100 kilos. of fatty matter 300 kilos. of good, bright, hard soap.

The manufacture of cocoa-nut oil soap resembles that of the other kinds of soap. With a weak ley cocoa-nut oil does not form the emulsion common to other soaps, but swims on the surface as a clear fat; when, by boiling, the ley has reached a proper consistence, the oil suddenly saponifies. A strong soda-ley is used in the preparation of this kind of soap. Cocoa-nut oil in saponifying does not separate from the under-ley, therefore potash-ley is never employed. To prevent the separation of the soap from the mixing, the quantity of caustic-ley used must be accurately measured. Pure cocoa-nut oil soap hardens quickly. It is white, like alabaster, shiny, soft, and easily lathered; it has, however, a peculiarly unpleasant smell, which cannot be entirely masked by any perfume. Cocoa-nut oil is seldom used alone, but usually as an addition to palm-oil and tallow. This kind of soap can be made without boiling, by merely heating to 80° C., by means of steam, to melt the fats, a strong soda-ley being added, and the mixture quickly stirred. This is known as the "cold method," and soap can be thus prepared in large quantities in a short time, and is generally hard and dry. When exposed to the air for a month or so, the soap loses considerably in weight, and becomes effloresced superficially. B. Unger (1869) prepares a soap in the following manner:—He saponifies palm-oil with soda-ley and salt as usual. The product is palmitate of soda. At the same time cocoa-nut oil is saponified by means of carbonated and caustic soda-ley; this is added to the palm-oil soap, and they are boiled. As a rule there are taken 2 parts of palm-oil to 1 part of cocoa-nut oil; and to 100 parts of the latter there are added 14·3 parts of caustic soda (Na_2O) and 12·8 parts of carbonate of soda. According to Unger's experiments, this soap contains 5 mols. palmitate of soda, 1 mol. carbonate of soda, and x mol. water. The "marbling" or "mottling" is effected in the following manner:—Colouring matters, oxide of iron, brown-red, Frankfort-black, are mixed with a small portion of soap; this is poured into the rest of the soap, with which it forms layers of unequal thickness. The entire mass is now stirred, and by this means a marbled or grained appearance imparted.

Soft-Soap. As before mentioned, potash forms with fats and oils only a *soft*-soap, which does not dry when exposed to the air, but on the contrary absorbs water, remaining constantly like a jelly. As a rule, these so-called soaps are impure solutions of oleate of potash in an excess of potash-ley, mixed with the glycerine separated in the saponification. Soft-soaps can be prepared only with potash-leys, although in practice 1 part of soda-ley is substituted for a part of the potash to assist in somewhat hardening the soap. There is no separation of the soap from the under-ley, which contains all the impurities; consequently these are disseminated in the soap.

In consequence of the solubility and cleansing properties of soft-soap, its use is preferred to that of soda-soap in the manufacture of cloth and woollen articles. It will have been seen that the difference in manufacturing hard- and soft-soaps consists in employing potash-ley for the latter, and soda for the former. Wood-ash is not used in preparing the potash-ley, but always pure potash; the preparation follows the usual method with caustic lime. The fats used are mixtures of the vegetable and animal oils, as the fish-oil known as "Southern," with rape, hemp, and linseed oils. The particular oil used varies according to the time of the year and market price: in winter the soft ones are employed; in summer the firmer oils. Soft-soap is generally used for fulling and scouring; but abroad it is sometimes used for washing linen, to which it imparts a most disagreeable fishy odour, hardly concealed by any amount of perfume. The best soft-soap is made from hemp-seed oil, this oil imparting a green tinge, which, however, can be imitated by adding indigo to inferior soaps. Summer soap, as it is termed, contains, owing to the fat employed, more palmitate of potash in proportion to oleate than the winter soap. Sometimes saponification is effected with a mixture of hemp- and palm-oil or tallow, of train-oil and tallow, &c.

The boiling of the soft-soap commences with a strong ley containing 8 to 10 per cent. potash, by which an emulsion is formed. The scum is dashed about with a stick, the beating-stick, and by this means all the alkali is caused to be taken up. A fresh ley is then added, and the boiling continued, until the soap upon cooling stiffens into a clear tough mass. When the soap contains too much caustic alkali, which can be ascertained by the taste, more oil is added. The *clear-boiling* now commences, during which the excess of water is removed. To avoid lengthy evaporation a concentrated ley is employed, and the soap, instead of bubbling up, has its surface covered with blisters as large as the hand; these blisters are termed leaves. When the boiling is finished—ascertained by placing some of the soap to cool on a glass plate, from which, if firm, it can be separated—the soap is cooled, and stored in barrels.

Soft-soap will take up a considerable quantity of water-glass solution without alteration. Recently, for fulling, there has been added to the soft-soap a solution of sulphate of potash, or a mixture of alum and common salt and also potato-starch.

Various other Soaps. Another soap is prepared from hog's-lard, and when scented with oil of almonds or essence of mirbane (nitrobenzol) is sold as almond-soap, and as a cosmetic. A soap is made from the grease of sheep's-wool. The so-called bone-soap is nothing more than a mixture of the usual hard or cocoa-nut oil soap with the jelly from bones. The bones are first treated with muriatic acid to separate the phosphate of calcium. A variety of bone-soap is the Liverpool common soap. Flint-soap is an oil- or tallow-soap with which siliceous earth is mixed. When powdered pumice-stone is substituted for the siliceous earth, the soap is called *pumice*-soap. In America as well as in England a water-glass solution is substituted for the siliceous earth, although according to Seeber the result is not so efficacious. Cocoa-nut oil soap, however, containing 24 per cent. silicate of soda and 50 per cent. water, is very firm. In the United States water-glass is added to the soap when, still hot from the boiling-pan, it is poured into the moulds. The water-glass solution is of a density = 35° B. (= 1·31 sp. gr.); the proportion of soap is 60 per cent. This kind of water-glass soap generally sets hard. Recently cryolite and aluminate of soda have been employed.

Toilet Soaps. On account of the reduction in the duty toilet soaps are now very largely in demand. They are generally made by re-melting and perfuming common soap. English toilet soap is considered the best, as that of France and Germany being perfumed while cold is not so equable a product.

There are three modes of preparing toilet soap, viz.:—

1. By re-melting raw soap;
2. By the cold perfuming of odourless soap;
3. By direct preparation.

1. In the method of re-melting, good raw soap is scraped into a boiling pan, and after melting and skimming the perfume is added. The soap is then cast in moulds of the required form. 2. In the method of perfuming in the cold, odourless soap is cut into fine shreds by a machine; the perfume is then added, and the soap is

passed between rollers, the sheets or bars thus formed being cut into tablets. Struve, of Leipsic, has invented a machine by means of which soap is stamped into the shape required. 3. The direct preparation of toilet-soap consists in colouring and scenting pure white common soap without an intervening cooling. The colouring materials are—for red, cinnabar, coralline, and fuchsine; the violet tar colour for violet; for blue, ultramarine; for brown, a solution of raw sugar or caramel. Windsor soap is prepared in the following manner:—40 pounds of mutton tallow and 15 to 20 pounds of olive-oil are mixed with soda-ley marking 19°, making a soap of 15°; finally, with ley marking 20°, when the soap is of the consistency of marrow. The excess of ley is then neutralised. When the soap is set it is allowed to stand six to eight hours, and during this time most of the under-ley separates. It is then placed in a flat form, and pressed until no fluid exudes. It is scented with cumin oil, bergamot, oil of lavender, oil of thyme, &c. Moist sugar is used to impart the brown colour. Rose soap, *savon à la rose*, is manufactured by melting the ingredients of three parts of oil-soap with two parts of tallow soap, and sometimes water; the perfume is attar of roses, oil of roses, or gilliflower-water, the colouring matter being generally cinnabar. Shaving-soap must not contain free alkalies. It is sometimes prepared by boiling fat acids with a mixture of the carbonates of soda and potash. Lather-soaps have in equal volume only half the substance of the other soaps. Palm- or olive-oil soap is melted with an addition of one-third to one-eighth the volume of water, and the mass stirred until it has increased to double the volume. It is then placed in a mould. It should be remarked that the oil-soaps, and not tallow-soaps, are the true formatives of the lather-soaps.

Transparent Soap. Ordinary dry tallow-soap is cut into splinters and heated with an equal weight of alcohol, in which the soap dissolves. The mixture is allowed to cool; therewith all impurities are thrown down, and the clear fluid is placed in the moulds, where it has to remain three to four weeks to harden. Tincture of cochineal and aniline red are employed for colouring transparent soaps, and also Martin's yellow. The perfume is chiefly oil of cinnamon, sometimes oil of thyme, oil of marjoram, and sassafras-oil. Glycerine-soap is prepared from an alcoholic solution of ordinary soap, to which glycerine is added. Or 5 cwts. of soap with an equal quantity of glycerine are heated by steam in a copper vessel. The mixture is placed in moulds, and allowed to set in the usual manner. A solution of soap in an excess of glycerine (35 : 30) forms fluid glycerine-soap, which is of a clear honey consistency. Both varieties are perfumed with essential oils.

Uses of Soap. Soap is used for cleansing purposes in washing, in bleaching cloth and woollen materials; for the preparation of lithographic tints, &c. The cleansing properties of soap are due to the alkalies it contains. The alkali, although combined with the fat acids, loses none of these properties, which are in fact included in the combination of the alkali with the fatty substances of the dirt to be removed. The explanation of the action chemically, according to Chevreul, is the following:—The neutral salts formed by the alkalies and the fat acids, stearates, palmitates, and oleates are decomposed by the water, whereby insoluble double fat acid salts are separated, while the alkali is set free. By means of the free alkali the impurities clinging to the materials are removed, and taken up by the fat acid salts, the suspended dirt being thus contained in the lather.

Soap Tests. The greater the quantity of fat acids combined in the soap, the higher is its value. A normal soap, besides alkaline fat acids, should only contain free water, the quantity of which gives a means of estimating the value of the soap. It is in the power of the soap-maker to manufacture 300 parts of a good hard soap out of 100 parts of fat. When too small a quantity of water is contained the soap becomes too hard, and much labour is lost in obtaining a lather. If, on the other hand, water is held in too large a quantity there is a great loss of material. The degree of hardness of the soap forms, therefore, another means of estimating its value. Many soaps contain 2 to 3 per cent. glycerine. But the proportion of water and the hardness of a soap are not the only means of estimation, there still remains the estimation of the neutral fat acid alkalies, the free alkali, common salt, or unsaponified fat in the residue left after the drying of the soap. According to W. Stein, the presence of free alkali may be ascertained by means of calomel, or according to Naschold, by nitrate of protoxide of mercury. Uncombined fat retards the formation of a lather, and after a time imparts to the soap a rancid odour. But the worth of a soap can only be accurately ascertained by means of chemical analysis.

Insoluble Soap. All soaps that have not potash or soda for a base are insoluble in water. Many of the insoluble soaps are of technical importance.

Calcium-soap plays an important part in stearine-wax manufacture. It is made either directly by saponifying fat with hydrate of lime, or by treating soluble soap with a solution of a salt of lime; this soap is formed to some extent when ordinary soap is dissolved in hard water. Barium- and strontium-soap are similar to calcium-soap. Magnesium-soap is made directly with difficulty; it may be obtained indirectly by dissolving ordinary soap in sea-water. Aluminium-soap is without doubt an insoluble soap; argillaceous earths will not saponify fat unless aluminate of soda or potash is present. Aluminium soap is used in waterproofing. According to Jarry, wood impregnated with oleate or stearate of aluminium is impervious to moisture. Lately many materials have been rendered waterproof by being dipped into a solution of acetate of aluminium, and then into a soap solution, aluminium soap being thus formed.

Manganese-soap is prepared by the addition of sulphate of manganese to ordinary soap, or by boiling carbonate of manganese with oleic acid. It is usually applied as a siccative. Zinc-soap is prepared by the double decomposition of sulphate of zinc and soap, or by the saponification of zinc-white with olive-oil or fat, forming a yellow-white mass. Zinc-soap is used as an oil-colour, and also as zinc-plaster. Lead-soap or lead-plaster is made by adding white-lead to olive-oil, or acetate of lead to soap solution. Tin-soap is prepared by the double decomposition of chloride of tin with soap. Copper-soap, formed by the addition of sulphate of copper solution to soap, is soluble in ether and oil, less so in alcohol; it is used in preparing water-colours. It may be made by boiling oleic acid with carbonate of copper. Mercury or quicksilver-soap is prepared from chloride of mercury and soap; it is difficult to dry; is white, but when exposed to air and light turns grey. Mercury-soap was formerly known as quicksilver-soap and quicksilver-plaster. Silver, gold, and platinum-soaps, are severally prepared by double decomposition; but they are not much used. Gold-soap is employed in gilding porcelain; and silver-soap for darkening the hair.

Boric or Boracic Acid, and Borax.

Boracic acid occurs native as sassolin, H_3BO_3; in 100 parts:—

Anhydrous boracic acid, B_2O_3	56·45
Water	43·55
	100·00

and further in the following minerals:—

Boracite. or borate of magnesium with chloride of magnesium	with	62·5	per cent.	Boracic acid.
Rhodicite, or borate of calcium	,,	30 to 45	,,	,,
Hayescine, Tiza, or borate of lime	,,	30 to 44	,,	,,
Hydroboracite	,,	47	,,	,,
Tincal or borax, borate of soda	,,	36·53	,,	,,
Datholite, or boro-silicate	,,	18	,,	,,
Botryolite	,,	20·35	,,	,,
Axinite	,,	2 to 6·6	,,	,,
Tourmaline	,,	2 to 11·8	,,	,,

Boracic acid is found also in small quantities in many mineral waters and in sea-water. Larderellite, or borate of ammonia, and lagonite, or borate of iron, are both found in very small quantities in Tuscany, but are interesting to mineralogists only.

Boracic acid is found as sassolin in many volcanic regions mixed with sulphur, and in the hot springs of Sasso, in Tuscany, and also between Volterra and Massa Maritima in the clefts and rents of the volcanic formation of rock. Höffer and Mascagni (1776), first mentioned the occurrence of boracic acid in the waters subjected, in the clefts of the rock, to the sulphurous exhalations. The little pools formed in these clefts are variously known as *fumacchi*, *fumaroles*, *soffioni*, and *mofetti*. The boracic acid deposits in some cases cover an extent of six miles. Since 1818 artificial soffioni have been constructed, and the benefit derived by the country from the introduction of the industry is immense. The first artificial lake was situated near Monte Cerboli, and the product was for some time known as Larderellite, from the owner's name, Larderel. The production from these works alone amounted in 1839 to 717,333 kilos., and in 1867 to 2,350,000 kilos. The increase has been greatest since 1854, owing to the energy with which Gazzeri and Durval entered upon the construction of the artificial soffioni.

The soil of the natural lakes, or beds of the natural soffioni, are of a slimy formation, and have a peculiar seething movement due to the escape of the sulphurous vapours from the fumaroles or vents. According to Payen, this vapour or steam may be considered as condensed and as non-condensed, the former containing besides water, sulphate of lime, sulphate of magnesia, sulphate of ammonia, chloride of iron, hydrochloric acid, organic substances, a fishy-smelling oil, clay, sand, and a small quantity of boracic acid. The non-condensed vapour consisted of—

Carbonic acid	0·5730
Nitrogen	0·3480
Oxygen	0·0657
Sulphuretted hydrogen	0·0133

Payen is of opinion that the vapours contain no boracic acid, while C. Schmidt thinks otherwise, as the vapours, when condensed without contact with the water of the soffioni, yield boracic acid. The condensed vapours contain 0·1 per cent. boracic acid.

Theory of the Formation of the Native Boracic Acid. Dumas and Payen found an explanation of the formation of volcanic boracic acid upon the hypothesis that there exists in the interior of the volcano or beneath the under-crust of the earth a layer of sulphide of boron (B_2S_3), which under the action of the mineral waters becomes converted into boracic acid and sulphuretted hydrogen. P. Bolley gives the action as similar to that occurring in the formation of sal-ammoniac, a very common mineral in volcanic regions. Professor Becchi, of Florence, found nitride of boron (BN) in one of the under-strata, from which he prepared artificially by means of steam ammonia and boracic acid. Also Warrington (1854) and Popp (1870) attributed the appearance of boracic acid and ammonia in volcanoes to the decomposition of nitride of boron by evaporation. Recently (1862) Becchi has obtained boracic acid by the decomposition of borate of calcium in a stream of superheated steam.

The Production of Boracic Acid. The most general method of obtaining boracic acid is by the evaporation of the water of the natural or artificial soffioni. The water is either naturally or artificially introduced into the natural fumaroles, as these sometimes do not resupply themselves with sufficient rapidity. As soon as the water has absorbed a considerable quantity of the vapours it is removed and placed in a large masonwork cistern; this cistern is imbedded in the soil near the fumaroles, and the natural heat is sufficient to cause evaporation. The vapours are condensed in a wooden chimney. The separated impurities, gypsum, &c., remain in the cistern. As soon as the solution is of a sp. gr. = 1·07—1·08 at 80°, it is poured into leaden crystallising vessels where the boracic acid crystallises out. The mother-liquor is evaporated to dryness. It should be remembered that the entire operation is conducted with the assistance of the natural heat of the fumaroles only. Occasionally the boracic acid is only present in the natural waters to 0·002 of a part; and in these cases fuel must be used in the evaporation, which therefore entails the expense of carriage, as fuel is very scarce near the soffioni. Charcoal is generally used. But by this means an acid is obtained, containing about 70 to 80 per cent. hydrated boracic acid, with 10 per cent. impurities. Clouet removes the impurities by treatment with 5 per cent. of ordinary hydrochloric acid. Boracic acid for pharmaceutical purposes may be prepared by dissolving 1 part of borax in 4 parts of boiling water, and decomposing the solution with one-third part of sulphuric, or better with half part of hydrochloric acid of 1·2 sp. gr. The acid separates on cooling, and can be purified by crystallisation.

In 100 parts of commercial boracic acid from Tuscany, H. Vohl (1866) found:—

	1.	2.	3.	4.	5.
Boracic acid	45·1996	47·6320	48·2357	45·2487	48·1314
Water of crystallisation..	34·8916	35·6983	37·2127	34·9010	38·0610
Water	4·5019	2·5860	1·0237	4·4990	1·5240
Sulphuric acid..	9·6135	7·9096	8·4423	9·5833	7·8161
Silicic acid	0·8121	1·2840	0·6000	0·2134	0·0861
Sand	0·2991	0·5000	0·1000	0·7722	0·4154
Oxide of iron	0·1266	0·1631	0·0920	0·1030	0·0431
Protoxide of manganese..	0·0031	traces	traces	traces	traces
Alumina	0·5786	0·0802	0·0504	0·1359	0·1736
Lime..	0·0109	0·3055	0·5178	traces	traces
Magnesia	0·6080	traces	traces	traces	traces
Potash	0·1801	0·2551	0·5178	0·6140	0·4134
Ammonia	2·9891	3·5165	3·5169	3·7659	3·0890
Soda	0·0029	traces	traces	traces	traces
Chloride of sodium.. ..	0·1012	0·0595	0·0401	0·1671	0·0321
Organic substances and loss	0·0918	0·0101	0·0101	—	0·0449
	100·0000	100·0000	100·0000	100·0000	100·0000

Properties and Uses of Boracic Acid. Pure boracic acid crystallises in mother-of-pearl-like leaves, which at 100° C. lose half their water of crystallisation without melting, the other half being driven off at a red-heat. After cooling the anhydrous acid appears as a hard, transparent, brittle glass of 1·83 sp. gr. 1 part boracic acid dissolves in 25·6 parts water at 15° C., and in 2·9 parts at 100° C. At 8° a saturated solution has a sp. gr. of 1·014. It imparts a green colour to the flame of the spirit-lamp. In a chemical point of view it is similar to silicic acid. Boracic acid is largely used in the preparation of borax, for glazing porcelain, and mixed in a weak aqueous solution with sulphuric acid in the preparation of the wicks of stearine and paraffin candles. It is also used for colouring gold, for decorating iron and steel, in the preparation of flint-glass, and artificial precious stones. In 1859 boracic acid was used in the preparation of hydrated oxide of chromium, known under the name of Pannetier's-green, *Vert-Guignet*, &c.

Borax. Borax, or bi-borate of soda, when anhydrous according to the formula $Na_2B_4O_7$, contains in 100 parts:—

Anhydrous boracic acid (B_2O_3)	69·05
Soda (Na_2O)	30·95
	100·00

It is found native in Alpine lakes, on the snow-capped mountains of India, China, Persia, in Ceylon, and Great Thibet. It is found in large quantity at Potosi in Bolivia, where the *Borax Lake*, according to Moore's analysis (1870) contains in 1 litre of its water (sp. g. = 1·027), 3·96 grammes of borax. Pyramid Lake, Humboldt Co., Nevada, yields also large quantities. By the heat of the sun the water of the borax lakes is evaporated and the borax crystallises out, and is gathered and brought into commerce under the name of Tincal. It appears in small six-sided crystals, more or less smooth. The Clear Lake in California, to the north of San Francisco, yields daily 2000 kilos. of borax.

Formerly tincal was purified by washing in water containing soda to free the borax from adhering fatty substances which combine with the soda to form an almost insoluble soap. After the borax has been well washed it is dissolved in boiling-water; for each 100 parts of refined salts there are 12 parts of carbonate of soda. The solution is next filtered, and then evaporated to 18° to 20° B. It is now placed in wooden crystallising vessels lined with lead, where it is necessary to allow the fluid to cool gradually. Another method is to place the tincal in cold water, and to stir in 1 per cent. of caustic lime. The fatty substances are thus removed, combining with the lime to form an insoluble calcium soap. 2 per cent. of chloride of calcium is added to the fluid, which is next evaporated, and set to crystallise. Clouet recommends the powdering of the tincal, which is next mixed with 10 per cent. nitrate of soda, and calcined in a cast-iron pan, the fatty substances being thus destroyed. The calcined mass is dissolved in water, and the solution evaporated to crystallisation.

Borax from Boracic Acid. In 1818 the manufacture of borax from boracic acid was commenced, and since that time borax has sunk to three-fourths its former price. Both according to the proportion of water and the crystalline form, there may be considered two varieties of borax. 1. The ordinary or prismatic borax; 2. Octahedral borax. The prismatic borax ($Na_2B_4O_7 + 10H_2O$) contains in 100 parts:—

Boracic acid	36·6
Soda	16·2
Water of crystallisation	47·2
	100·0

The octahedral borax ($Na_2B_4O_7 + 5H_2O$) contains in 100 parts:—

Boracic acid Soda	69·36
Water	30·64
	100·00

Prismatic borax is manufactured in the following manner:—There are dissolved in a lead-lined vessel, A, Fig. 118, 26 cwts. of crystallised carbonate of soda in about 1500 litres of water, heated by means of steam, to the boiling-point. The boiler, C, is for the purpose only of generating steam, which is passed by the pipe, *c*, and the rose, *m*, into A.

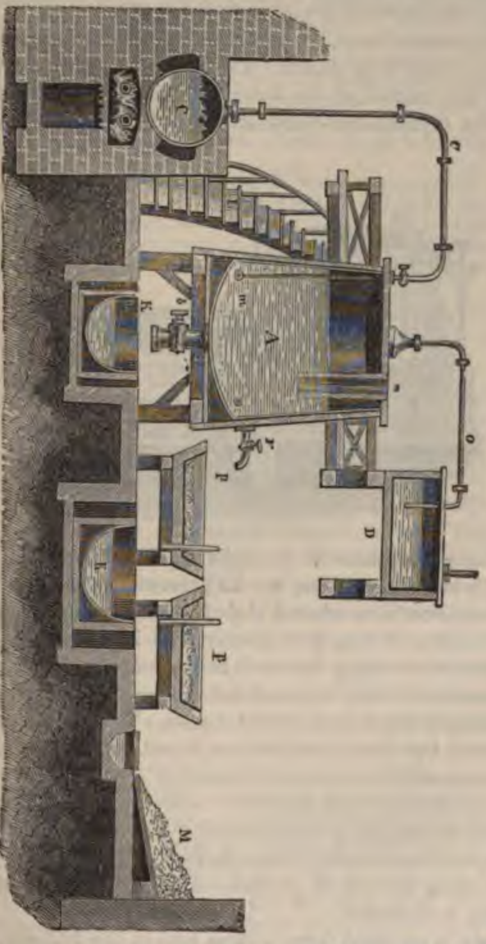
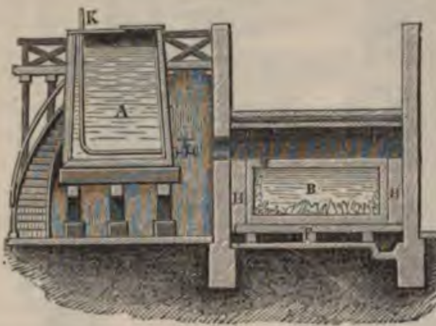


Fig. 118.

By means of the large taps, *b* and *r*, the fluid may be removed from A. Through the tube *a* the substances thrown down from the solution can be removed. Boracic acid is added in quantities of 8 to 10 lbs. after the solution has been heated to the boiling-point. Besides carbonic acid a small quantity of carbonate of ammonia is developed, and passes by *o* into the vessel D, containing dilute sulphuric acid, by which it is absorbed. To saturate the solution of 26 cwts. of soda, 24 cwts. of crude boracic acid are necessary. The boiling saturated solution marks 21° to 22° B., and has a temperature of 104°. If the solution is too strong, water is added; if too weak, a small quantity of crude borax, to bring it to 21° B. The solution is allowed to stand in A until all insoluble substances are deposited. The clear ley is conducted by means of the tap, *r*, into the crystallising vessels, P P, the mud or deposit being received into K. The crystallising vessels are of wood lined with lead. The crystallisation is complete in two to three days, and the mother-liquor is drawn off into the vessel H. The crystals are placed to drain on the inclined plane, M. The mother-liquor is retained for the dilution of a fresh quantity of soda. After three or four operations, the mother-liquor contains sufficient sulphate of soda to admit of profitable crystallisation; and the ley is allowed to cool at 30°. As the solubility of sulphate of soda has reached the maximum at a temperature of 33°, it is clear that the crystallisation of the sulphate commences at the completion of that of the borax. After the crystallisation of the sulphate of soda, the mother-liquor is evaporated to dryness, and the saline residue is sold to the glass-manufacturer.

Purifying the Borax. The crude borax to be purified is placed in a lead-lined wooden cistern, A, Fig. 119, heated by steam. The borax is suspended in a wire sieve immediately under the surface of the water with which A is filled. To 100 parts of borax, 5 parts of crystallised carbonate of soda are added, and the liquid is strengthened from time to time till it marks 22° B. When the solution is settled it is removed by the tap to the cooler, B. To prevent loss of ley, the floor under B is stippled with waterproof cement, and sloped towards a gutter. The crystallising vessel is of thick timbers, H F H, lined stoutly with lead; this vessel is filled with ley to within an inch of the edge, the cover being then placed on. The steam condenses on the cover, which when removed is found covered with small crystals, the larger crystals falling to the bottom of the vessel. To hasten the cooling, spaces are left in timbers, F; but the crystallisation is not effected under 16 to 28 days. After this time the ley still has a temperature of 27° to 28° C. When quite cool the foreign substances separate from the borax. The vessel, B, contains the large borax crystals from which the adhering mother-liquor is separated by a sponge. If the crystals are not thus carefully treated, they split into thin leaves; for this reason also the cooling should be gradual. The crystals are dried on a wooden table, finally sorted, and packed.

Fig. 119.



In England borax is prepared from boracic acid in the following manner:—The crude boracic acid is mixed with half its weight of calcined soda and submitted to the action of heat in a muffle-oven. The ammonia, which as sulphate is an important constituent of crude boracic acid, is, with carbonic acid, given off during the process, and passes through a tube to a condensing chamber. The melted mass is removed, and lixiviated in an iron pan; the suspended matter is allowed to settle, and the clear liquor is put into smaller vessels to cool, in which beautiful crystals form. It has already been mentioned that this manufacture had its origin in France, where sulphuric vapours were employed. A mixture of calcined Glauber salts and boracic acid were placed in a retort and subjected to distillation, the residue on lixiviation and crystallisation yielding borax. Köhnke substitutes caustic soda for the carbonate of soda, the borax crystallising from a very alkaline solution.

Recently borax has been obtained from native borate of calcium, *tiza* or borocalcite, (formula, according to Wöhler, $Na_2B_4O_7 + 2CaB_4O_7 + 18H_2O$), which occurs in large quantities at Tarapaca in Peru, and in Western Africa. Treatment with sulphuric acid gives only unsatisfactory results, and hydrochloric acid is therefore employed. The acid is poured upon the mineral to two-thirds of its weight with twice the quantity of water, and the whole heated to the boiling-point, and allowed to digest. The heat must be maintained to the completion of the digestion, and the water lost by evaporation re-supplied. The clear liquor is then decanted, and on cooling the boracic acid crystallises out, the mother-liquor retaining chloride of sodium, chloride of calcium, with a slight excess of hydrochloric acid. Stassfurt boracite or Stassfurtite, is also becoming largely used in the preparation of borax.

The prismatic borax is colourless and forms transparent crystals of 1·75 sp. gr., dissolved in 12 parts cold and 2 parts boiling water, the solution having a weak alkaline reaction upon test-paper, although borax is an acid salt. By exposure to the air it loses water. At a moderate heat it separates into a spongy mass known as calcined borax, and at a red-heat assumes a glassy appearance; in this condition it is used as a blowpipe flux.

Octahedral Borax. Octahedral borax ($Na_2B_4O_7 + 5H_2O$), is prepared in the following manner:—Prismatic borax is dissolved in boiling water till the solution marks 30° B. = 1·260 sp. gr. This solution is then allowed to cool very slowly. When the temperature has fallen to 79° C., the octahedral crystals begin to form, the formation continuing till the temperature reaches 56°. After this the mother-ley yields only prismatic crystals. Unless great care be taken, a mixed crystallisation results. Buran recommends the preparation of octahedral borax by evaporating a borax solution to 32° B. = 1·282 sp. gr., when it is removed to a crystallising vessel. When 10 cwts. of borax are operated upon, the process will take six days to complete. The prismatic and octahedral salt crystallises in distinct layers that can be separated mechanically. Indian borax and Chinese half-refined borax sometimes contain octahedral crystals. Octahedral borax is known in French commerce under the names of calcined borax, jeweller's borax, surface borax, &c. It is distinguished from prismatic borax by its crystalline form and the proportion of water contained, by its sp. gr. = 1·81, and its greater hardness. While the prismatic borax remains unaffected in transparency by exposure to air, the octahedral borax rapidly becomes opaque, and absorbing five equivalents of water is converted into the prismatic salt.

Uses of Borax. The uses of borax are very numerous. Molten borax has the property, at high temperatures, of fluxing metallic oxides, vitrifying with them into coloured transparent glasses; for instance, with protoxide of cobalt a blue glass is formed, and with oxide of chromium a green glass. This property is of great utility in chemical analysis, as the various metallic oxides may be thus distinguished in the blowpipe flame. It is also used for soldering metals; and is a constituent of *Strass*, used in glass-manufacture and enamelling. It is used extensively in glazing the finer kinds of earthenware, and for separating metals from their ores. Borax forms with shellac in proportion of 1 part to 5 parts of a peculiar varnish, soluble in water, and used when mixed with aniline black to stiffen felt hats. With casein its gives a fluid resembling a solution of gum-arabic, for which it is often substituted. Borax is made into a soap for washing purposes, into a solution for cleansing the hair, and it is also used in various cosmetics, &c. It is largely employed to fix mineral mordants. According to Clouet, a mixture of boracic acid and nitrate of potash or soda is in many cases a better flux than borax. He recommends 100 parts boracic acid and 100 parts of the nitrate to be placed in an enamelled iron kettle with 10 per cent. water and heated till fluid. When cooled, flat white crystals are formed; those made with nitrate of potash can be used for crystal-glass manufacture, and those with nitrate of soda for enamelling. Borate of chromium is known in commerce as *Vert-Guignet* or Pannetier's green.

Diamond-Boron, or Adamantine. Wöhler and H. Deville in 1857 were the first to notice that boron forms similarly to carbon in two allotropic conditions, namely, crystalline* and amorphous. Diamond boron is prepared in two ways, either by the reduction of calcined borax with aluminium:—

$$\left.\begin{array}{l}\text{Boracic acid, } B_2O_3,\\ \text{Aluminium, } 2A,\end{array}\right\} \text{ yields } \left\{\begin{array}{l}\text{Alumina, } Al_2O_3,\\ \text{Boron, } 2B;\end{array}\right.$$

or by converting amorphous boron into crystalline. The latter method gives the better result. 100 grms. of anhydrous boracic acid are mixed with 60 grms. of sodium in a small iron crucible heated to a red-heat. To this mixture 40 to 50 grms. of common salt are added, and the crucible is luted down. As soon as the reaction is finished, the mass, consisting of amorphous boron with boracic acid, borax, and common salt intermingled, is stirred into water acidified with hydrochloric acid. The boron is filtered out, washed with a weak solution of hydrochloric acid, and placed upon a porous stone to dry at the ordinary temperature. Molten iron, it is well known, converts amorphous carbon into crystalline graphitic carbon, and aluminium exercises a similar action upon boron. The crystalline boron is prepared in the following manner:—A small crucible is filled with amorphous boron, in the centre of which a small bar of aluminium weighing 4 to 6 grms. is placed. The crucible is submitted to a temperature sufficient to melt nickel for 1½ to 2 hours. After cooling the aluminium will be found covered with beautiful crystals of boron. The diamond boron is easily separated from the graphitoid. The form is a transparent tetragonal crystal, of a garnet-red or honey-yellow colour, or, if perfectly pure, colourless. It is very brittle, hard, and lustrous; it will scratch rubies easily. This discovery may in time be of great technical importance.

PRODUCTION OF ALUM, SULPHATES OF ALUMINA, AND ALUMINATES.

Alum. Alum is a saline substance, consisting of sulphate of alumina, sulphate of potash or ammonia, and water of crystallisation. It occurs native as potash-alum and as ammonia-alum, being, in fact, a double salt, consisting of either sulphate of alumina and sulphate of potash, or sulphate of alumina and sulphate of ammonia. The alum known as potash-alum, $\left.\begin{array}{c}Al_2\\ K_2\end{array}\right\} 4SO_4 + 24H_2O$, is found in alum-shale. But all natural alums are of more mineralogical than technical interest, the alums of commerce being always artificially prepared. We shall, therefore, pass on to the consideration of the latter.

Material of Alum Manufacture. The manufacture of alum grounds itself on the formation of sulphate of alumina and aluminate of soda from the various alum-ores. These ores or earths necessitating different methods of treatment, may be divided into four groups, viz.:—

1. Those which contain alumina, potassa, and sulphuric acid in such proportions that the addition of an alkaline salt is not requisite. To this group belongs alum-stone, and several varieties of alum-shale.

2. Those in which the sulphate of aluminia is alone present, necessitating the addition of alkali salts in large quantities. To this group belong the alum-shale and alum-earths found in the brown-coal formation.

3. Those in which alumina only is contained, and to which both sulphuric acid and alkali salts must be added. To this group belong—α. Clay; β. Cryolite; γ. Bauxite; δ. Refuse slack.

4. To the fourth group belong those materials, such as felspar, containing alumina and potash in sufficient quantity, but needing the addition of sulphuric acid.

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* Graphitic boron is by a later discovery of Wöhler's (1867) resolved into boracic-aluminium; formula, AlB_2.

Preparation of Alum from Alum-stone. 1st *Group.*—Alum-stone or alunite occurs only in volcanic regions, and is the product of the action of the sulphurous vapours upon substances rich in felspar. It is found at Talfa, near Civita-Vecchia, and in large quantities at Muszag, in Hungary. The crystallised alum-stone consists of sulphates of potash and alumina with hydroxide of aluminium, according to Al. Mitscherlich—$K_2SO_4 + Al_2(SO_4)_3 + 2(Al_2O_3, 3H_2O)$.

Alum-stone loses its water at a red-heat, the product of the calcination being influenced by water, while unburnt alum-stone is not. At a strong red-heat the sulphate of alumina separates into alumina, sulphurous acid, and oxygen, and the sulphate of potash is also decomposed. The mineral is calcined in lime-kilns in the ordinary manner. The calcined alum-stone is lixiviated with boiling water, the supernatant liquor decanted, and the alum crystallised out. Roman rock, or roche alum is prepared in a similar manner, the red colour being due to peroxide of iron.

Preparation of Alum from Alum-shale and Alum-earths. 2nd *Group.*—This mode of preparation yields the greatest amount of alum with as much facility as from alum-stone.

Alum-shale. Alum-shale or schist is a sulphurous iron pyrites, found under beds of clay in Upper Bavaria, in Prussia, near Dusseldorf, Saxony, Bohemia, Belgium, &c. Only very inferior kinds require an addition of alkali salts.

Alum Earths. Alum-earth is more or less a mixture of sulphurous iron pyrites with various bitumnious matters. The sulphur is present partly in free state, partly as iron and vitriol pyrites; the iron is present partly as sulphuret, partly as iron humate.

Preparation of Alum. The preparation of the alum may be considered in the following six operations:—

Roasting the Alum-Earth. 1. The roasting of the alum earths is the easiest of the operations. The greater part of the alum manufactured is produced by precipitating sulphate of alumina with a solution of alkali salts. It is not always necessary the schist should be burnt to concentrate the sulphate of alumina, a lengthy weathering being sufficient. The action may be explained as follows:—By the weathering the bisulphide of iron absorbs oxygen, to form sulphate of iron, which separates into protoxide of iron and sulphuric acid, the latter acting upon the alumina forming an equivalent quantity of sulphate of alumina. Or by roasting, the bisulphide is decomposed to monosulphide and sulphur, which, with the sulphur of the alum-earth, gives rise to sulphurous acid, and this acting upon the alumina produces sulphite of alumina and also the sulphate. The roasting or calcination, however, should not take place with earths that have been subjected to less than a year's weathering, as there is found to be in practice a loss of one-sixth of the sulphate of alumina.

Lixiviation. 2. The lixiviation of the calcined alum earths is effected in a lixiviation cistern in which the earth is placed. These tanks stand in rows of five, the best arrangement being to build them on a slope near the calcination heaps. Each vessel has a length of 6 to 7 metres, is 5 metres broad, and about 1·3 metres in height. They are three-parts filled with the burnt earth, and completely with water; the lixivium flows from the highest tank to the lowest. If the ley is not of 1·16 sp. gr. fresh shale is added.

Evaporation of the Ley. 3. The concentration of the raw ley by evaporation is accomplished in leaden pans. These, however, deteriorate, crack, are easily melted, and their place is now generally supplied by cisterns of masonry. But most to be preferred is Bleibtreu's method of heating with gas, introduced in the alum-works on the banks of the Rhine. The treatment of the raw ley while being concentrated depends upon its condition and upon the sulphate of iron it contains. As sulphate of iron is commonly present in large quantities in the raw ley or liquor, many of the German alum-works are also vitriol-works. When, however, the quantity of sulphate of iron is too small to admit of being advantageously treated for the preparation of sulphate of iron, the liquor is at once evaporated until it has attained a sp. gr. of 1·40. During the ebullition basic sulphate of iron is deposited, the liquor becomes of yellow-red colour, assumes a somewhat slimy condition, and has to be rendered clear before alum is obtained from it. This clearing is effected by pouring the liquor into large wooden water-tight tanks; the liquor having deposited, the suspended matter is tapped or syphoned off from the sediment, and transferred to the precipitation tanks.

Alum-Flour. 4. The precipitation of flour of alum is effected in case it is desired to make potash-alum by the addition to the liquor of a potash salt, or of an ammonia salt if it is desired to make ammonia-alum. The solution of the alkaline salt is called the precipitant; by the combination of the sulphate of alumina contained in the liquor with the precipitant alum is formed, and deposited as a solid salt, care being taken to prevent the formation of large crystals by keeping the liquid stirred. By this means the alum is deposited as a crystalline powder or so-called flour of alum, which by being washed with cold water can be freed from any adhering mother-liquor. The precipitation was formerly effected by the addition of wood-ash ley or lant; at the present day chloride of potassium obtained either from kelp, carnallite, or beet-root molasses, and sulphate of potassa derived from the decomposition of kainite, are employed for this purpose. Chloride of potassium is useful only when the solution contains large quantities of sulphate of iron, which being converted into chloride of iron forms sulphate of potassa. Potash can only be used when the ley contains enough free sulphuric acid to combine with the salt, for otherwise a portion of the sulphate of alumina would become precipitated as insoluble alumina. The ammonia salt made use of is generally sulphate of ammonia; 100 parts of sulphate of alumina require for precipitation—

Chloride of potassium	43·5 parts
Sulphate of potassa	50·9 „
Sulphate of ammonia	47·8 „

The liquor covering the alum-flour is somewhat of a green colour, and contains little alum, but chiefly proto-perchloride of iron, sulphates of iron, sulphate of magnesia, or chloride of magnesium, dependent upon whether the precipitation was effected by sulphates or by chlorides. This liquor is used for making impure alum, sulphate of iron, or is employed in the preparation of sulphate of ammonia.

Washing and Re-crystallisation. 5. The floury alum is generally washed in the hydro-extractor or centrifugal machine and the liquor obtained again used for preparing alum. The washed floury alum is (6) converted into large crystals by re-crystallisation, the alum at the same time being purified. For this purpose the alum flour is dissolved in 40 per cent. of its weight of boiling water, the operation being carried on in wooden lead-lined tanks. The hot solution is run into crystallising vessels, where the crystallisation is finished according to the temperature of the air in eight to ten days. From this operation hardly any mother-liquor remains, the vessel being almost entirely filled with alum crystals.

Preparation of Alum from Clay. *3rd Group.*—The manufacture of alum and of sulphate of alumina from such materials as contain only alumina, to which consequently sulphuric acid and alkaline salts have to be added, has come largely into practice in England. The materials employed are:—α. Clay; β. Cryolite; γ. Bauxite; δ. Blast-furnace slag.

α. *Preparation of Alum from Clay.*—The clay to be employed for this purpose should be as free as possible from carbonates of lime and iron. It is first gently heated in contact with air, partly with the view of dehydratation, partly for the purpose of converting any iron into oxide, and lastly to render the clay more readily soluble in acids. By dehyadratation the clay becomes porous and fit to take up sulphuric acid by capillarity. The gently ignited and powdered clay is gradually put into sulphuric acid of 50° B. (=1·52 sp. gr.) contained in a leaden pan, and heated nearly to the boiling-point. The mass effervesces and becomes thick, and is next transferred to iron tanks, where it solidifies. It is afterwards lixiviated with water, or better, with the liquor obtained by washing the alum-flour. The lixivium having become clear by standing is syphoned off from the sediment, and boiled with a sufficient quantity of bisulphate of potash or sulphate of ammonia from gas-liquor. The hot solution is transferred to a shallow leaden pan, and kept stirred for the purpose of converting the alum on solidifying into flour. The flour is washed, dried, and is then converted into large crystals as described above. The product known in the trade as alum-cake is the result of the action of sulphuric acid upon clay; it is met with in a pulverised state, is used more especially in the manufacture of inferior kinds of paper, and contains from 13 to 17 per cent. of alumina.

Preparation of Alum from Cryolite. β. Since the year 1857 alum and sulphate of alumina have been prepared along with soda, from the mineral known as cryolite or Greenland spar, $Al_2Fl_6+6NaFl$, and consisting in 100 parts of—

Fluorine	54·5
Aluminium..	13·0
Sodium	32·5

The following are the methods employed for this purpose:—

a. Decomposition of Cryolite by Ignition with Carbonate of Lime according to Thomsen's Method.—1 molecule of cryolite is ignited with 6 molecules of carbonate of lime, carbonic acid escapes, and soluble aluminate of soda, and insoluble fluoride of calcium are formed $(Al_2Fl_6,6NaFl)+6CaCo_3=Al_2O_3,3Na_2O+6CaFl+6CO_2$. From the ignited mass the aluminate of soda is obtained by lixiviation with water, and into the solution carbonic acid gas is passed. The result is the precipitation of hydrated gelatinous alumina and carbonate of soda, which remains in solution. If it be desired to obtain the alumina as an earthy compact precipitate, bicarbonate of soda is used as a precipitant instead of carbonic acid. While the clear liquor is boiled down for the purpose of obtaining carbonate of soda, the precipitated alumina is dissolved in dilute sulphuric acid; this solution is evaporated for the purpose of obtaining sulphate of alumina (so-called concentrated alum), or the solution after having been treated with a potassa or ammonia salt is converted into alum. 100 lbs. of cryolite yield 33 lbs. of alumina, which require 90 lbs. of sulphuric acid to yield a neutral solution; 100 lbs. of cryolite will therefore yield 305 lbs. of alum, and may give in addition:—

Calcined soda	75·0 lbs., or
Crystallised carbonate of soda	203·0 „ or
Caustic soda	44·0 „ or
Bicarbonate of soda..	119·5 „

b. Decomposition of Cryolite with Caustic Lime by the Wet Way (Sauerwein's Method).—Very finely ground cryolite is boiled with water and lime, the purer the better, and as free from iron as possible, in a leaden pan. The result is the formation of a solution of aluminate of soda and insoluble fluoride of calcium.

$$(Al_2Fl_6,6NaFl)+6CaO=Al_2O_3,3Na_2O+6CaFl_2.$$

When the fluoride of calcium has been deposited, the clear liquid is decanted, and the sediment washed, the first wash-water being added to the decanted liquor, and the second and third wash-waters being used instead of pure water at a subsequent operation. In order to separate the alumina from the solution of aluminate of soda, there is added to the liquid while being continuously stirred, very finely pulverised cryolite in excess, the result of the decomposition being exhibited by the following formula:—

$$(Al_2O_3,3Na_2O)+(Al_2Fl_6,6NaFl)=2Al_2O_3+12NaFl.$$

When no more caustic soda can be detected in the liquid—a small quantity of which should, after filtration, yield, upon the addition of a solution of sal-ammoniac and application of heat, a precipitate of alumina—it is left to stand for the purpose of becoming clear. The clarified solution of fluoride of sodium is then drawn off, and the alumina treated as above described. The solution of fluoride of sodium having been boiled with caustic lime yields a caustic soda solution which, having been decanted from the sediment of fluoride of calcium, is evaporated to dryness. Recently the fluoride of calcium obtained as a by-product of the cryolite industry is used in glass-making.

c. The decomposition of cryolite by sulphuric acid yields sulphate of soda, convertible into carbonate by Leblanc's process, and sulphate of alumina free from iron. 238 parts of cryolite require for decomposition 240 parts of anhydrous or 321 parts of ordinary sulphuric acid. The resulting compounds are sulphate of alumina, sulphate of soda, and hydrofluoric acid:—

$$\left.\begin{array}{l}Al_2Fl_6 6NaFl,\\ 6H_2SO_4,\end{array}\right\}\ \text{yield}\ \left\{\begin{array}{l}Al_2(SO_4)_3.\\ 3Na_2SO_4.\\ 12HFl.\end{array}\right.$$

This method of decomposing cryolite is, however, by no means to be recommended, as owing to the liberation of hydrofluoric acid, peculiarly constructed apparatus are required; while the sulphate of soda has to be converted into carbonate of soda. Persoz suggests that cryolite should be treated in platinum vessels with three times its weight of strong sulphuric acid, to be recovered with the hydrofluoric acid by distillation. The solid residue should be treated with cold water in order to dissolve the larger part of the bisulphate of soda contained in the saline mass, from which the anhydrous sulphate of alumina is extracted with boiling water, and converted by the addition of sulphate of potassa or ammonia into alum free from iron. The solution of bisulphate of soda having been evaporated to dryness, is employed for the preparation of fuming sulphuric acid, Glauber's salt remaining as a residue.

Preparation of Alum from Bauxite. γ. In some parts of Southern France, in Calabria, near Belfast, Ireland, and other parts of Europe, a mineral occurs, consisting essentially (60 per cent.) of hydrated alumina of greater or less purity, termed bauxite, from the fact of having been first found in the commune of Baux, in France. In order to prepare alum and sulphate of alumina from this mineral it is first disintegrated by being ignited with carbonate of soda, or with a mixture of sulphate of soda and charcoal; in each instance the lixiviation of the ignited mass yields aluminate of soda, from which, by processes already described under Cryolite, alum, or sulphate of alumina, and soda are prepared.

Preparation of Alum from Blast-Furnace Slag. 8. J. Lürmann recommends that the slag be decomposed by means of hydrochloric acid. From the resulting solution of chloride of aluminium the alumina is precipitated by carbonate of lime, any dissolved silica being precipitated at the same time. The alumina is dissolved in sulphuric acid, leaving the silica. 100 kilos. of slag containing 25 per cent. of alumina yield 180 kilos. of alum and 31 kilos. of silica.

Alum from Felspar. *4th Group.*—The manufacture of alum from minerals, (for instance, felspar) containing alumina and potassa, is not of any industrial importance; we therefore refer the reader to what has been said (see page 122) on the Preparation of Potassa Salts from Felspar.

Properties of Alum. Potash-alum, $\left.\begin{matrix}Al_2\\K_2\end{matrix}\right\}4SO_4+24H_2O$, or $K_2SO_4+Al_2(SO_4)_3+24H_2O$, consists in 100 parts of:—

Potassa	9·95
Alumina	10·83
Sulphuric acid	33·71
Water	45·51
	100·00

crystallises readily in regular octhahedra, loses at 60° 18 mols. of water, and fuses at 92° in its water of crystallisation, yielding a colourless fluid which retains its state of aggregation for some time after cooling before solidifying into a crystalline mass. At a temperature a little below red heat alum loses all its water, becoming converted into burnt-alum, *alumen ustum*, a white, porous, readily friable mass. When ignited with carbonaceous matter, air being excluded, potash-alum forms a pyrophoric compound:—

100 parts of water	at	0°	dissolve	3·9	parts of potash-alum.
,,	,,	20°	,,	15·8	,, ,,
,,	,,	40°	,,	31·2	,, ,,
,,	,,	100°	,,	360·0	,, ,,

The solution of alum in water (the salt is insoluble in alcohol) has an astringent sweet taste, and possesses an acid reaction so strong that when alum is heated with common salt hydrochloric acid is evolved; while a concentrated solution of alum destroys the blue colour of many—not of all—artificial ultramarines.

Ammonia-Alum. This salt, $\left.\begin{matrix}Al_2\\(NH_4)_2\end{matrix}\right\}4SO_4+24H_2O$, or $(NH_4)_2SO_4+Al_2(SO_4)_3+24HO$, consists in 100 parts of:—

Ammonia	3·89
Alumina	11·90
Sulphuric acid	35·10
Water	48·11
	100·00

Ammonia-alum is now far more extensively manufactured than potash-alum. When ammonia-alum is strongly heated, sulphate of ammonia, water, and sulphuric acid are driven off, and alumina remains.

100 parts of water at 0° dissolve 5·22 parts of ammonia-alum.
„ „ 20° „ 13·66 „ „
„ „ 40° „ 27·27 „ „
„ „ 100° „ 421·90 „ „

Soda-Alum. The formula of this salt is—

$$\left.\begin{matrix}Al_2\\ Na_2\end{matrix}\right\} 4SO_4 + 24H_2O, \text{ or } Na_2SO_4 + Al_2(SO_4)_3 + 24H_2O$$

containing in 100 parts:—

Soda	6·8
Alumina	11·2
Sulphuric acid	34·9
Water	47·1
	100·0

It is as readily prepared from sulphate of alumina and sulphate of soda as the alums already mentioned, but its solubility prevents the separation from the mother-liquor, while its solution when boiled loses the property of crystallising. As iron cannot be removed from this salt by re-crystallisation, the materials it is obtained from should be free from that metal. The solutions should be mixed cold, and gently evaporated at a temperature not exceeding 60°.

Neutral or cubical alum ($K_2SO_4 + Al_2O_3,2SO_3$) is obtained either by adding to an alum solution so much carbonate of potassa or soda as will begin to separate the alumina, or a solution of alum is treated with gelatinous alumina. By boiling 12 parts of alum and 1 part of slaked lime in water, the same salt is obtained. This neutral salt is often preferred in dyeing and calico printing, as it does not affect certain colours. When ammonia-alum is similarly treated, it also yields a neutral alum. Blesser (*a*) and Schmidt (*b*) found the following to be the composition of cubical alum in 100 parts:—

	a.	*b.*
Sulphuric acid	34·52	33·95
Alumina	11·86	11.48
Potassa	9·44	9·04
Water	45·27	45·61
	101·09	100·08

Insoluble, or basic alum, $\left.\begin{matrix}Al_2\\ K_2\end{matrix}\right\} 2SO_4$, is obtained by boiling a solution of alum with hydrate of alumina; it is a white, insoluble powder, and as regards its composition similar to alum-stone. Basic alum is soluble in acetic acid.

Sulphate of Alumina. The active principle of alum is evidently the sulphate of alumina, not the sulphates of potassa and ammonia, the object of the preparation of the double salt being simply the obtaining of a definite compound, which, while it readily crystallises, can be obtained in a pure state, especially free from iron, a very injurious ingredent in alum used in dyeing and calico-printing. However, at the present day, with improved methods of manufacture, sulphate of alumina is largely prepared, and of excellent quality. It is often sold under the name of concentrated alum; and occurs in the trade as square cakes. It is white, somewhat transparent, and may be cut with a knife; is readily soluble in water, contains always free sulphuric acid, and also to some extent potassa, and soda-alum.

In the pure state this salt has the formula, $Al_2(SO_4)_3 + 18H_2O$, and contains in 100 parts—alumina, 18·78; sulphuric acid, 38·27; water, 42·95; total, 100. That the composition of this salt as met with in commerce varies greatly may be inferred from the following results of Varrentrapp's analyses of different samples of this salt:—

	1.	2.	3.	4.
Alumina	15·3	12·5	15·1	13·0
Sulphuric acid	38·0	30·6	38·0	34·0

According to the formula, the quantity of sulphuric acid in these samples should have been—

1.	2.	3.	4.
35·8	29·2	43·3	30·5

The quantity of water even varies between 56 and 48 per cent. for different parts of the same cake. Weygand found a sample of this salt prepared at Schwemsal to contain—alumina, 15·57; sulphuric acid, 38·13; oxide of iron, 1·15; potassa, 0·62; water, 45·79 parts. The sulphate of alumina prepared from cryolite at Harburg contains about 5 per cent. of sulphate of soda. The results obtained in the analyses by H. Fleck of various samples of sulphate of alumina are:—

Sulphate of alumina	47·35	50·80	51·63
Sulphate of soda	4·35	1·24	0·77
Free sulphuric acid	0·73	0·27	—
Water	47·37	47·47	46·94
	99·80	99·78	99·34

Sulphate of alumina is prepared either from clay, cryolite, or bauxite by methods already described. When clay is employed, the iron has to be removed from the dilute solution of the sulphate of alumina by precipitation as Berlin blue by means of ferrocyanide of potassium. When cryolite is used, the alumina, separated from the solution of aluminate of soda by carbonic acid, or powdered cryolite, is put into sulphuric acid, contained in a wooden lead-lined tank, and heated to 80° to 90°, the addition of the alumina to the acid being continued until solution ceases to take place. The solution having been clarified by standing for some time is next evaporated in a copper vessel until the salt fuses; it is then cast into moulds. With due care sulphate of alumina may be used in dyeing and calico-printing, but it cannot be altogether substituted for alum, owing to its variable composition.

Aluminate of Soda. Aluminate of soda is now prepared on the large scale, as it has been found to be a useful form of soluble alumina, especially in dyeing and calico-printing. The preparation of this compound is based upon the solubility of hydrate of alumina in caustic potassa or soda-ley, and the ready decomposition of the solution by carbonic and acetic acids, bicarbonate and acetate of soda, sal-ammoniac, &c.

Aluminate of soda was first brought under the notice of dyers by Macquer and Haussmann in 1819, but owing to the preparation being too expensive it did not come into industrial application until comparatively recently. We have already described the mode of manufacturing aluminate of soda from cryolite; but in Germany—the chief seat of cryolite industry—this salt is not made on the large scale; in France it is manufactured by Merle and Co., at Alais, and in England at the Washington Chemical Works. In France bauxite, containing 60 to 75 per cent. of alumina, and from 12 to 20 per cent. of oxide of iron, is the raw material, and is treated with caustic or carbonate of soda. If caustic soda is used the pulverised mineral is boiled with a solution of the alkali; while if the carbonate is employed the mixture is ignited in a reverberatory furnace. In either case aluminate of soda is produced, dissolved—in the case of ignition the semi-fused mass is lixiviated with water—and evaporated to dryness. The salt met with in commerce is a white powder with a green-yellow hue, dry to the touch, and consisting of—

Alumina	48
Soda	44
Chloride of sodium and Glauber's salt	8
	100

The formula, $\left.\begin{matrix}Al_2\\Na_6\end{matrix}\right\}O_6$ would require:—

Alumina	52·79
Soda	47·21
	100·00

Aluminate of soda is equally soluble in cold and hot water. Exposed to air it absorbs moisture and carbonic acid, and consequently on being dissolved in water the salt so changed yields a turbid solution, owing to alumina being suspended. The aqueous solution of this salt is not stronger than 10° to 12° B., = 1·07 to 1·09 sp. gr. According to Le Chatellier, Deville, and Jacquemart, sulphate of alumina is the starting-point of the preparation of the aluminate of soda by precipitating from the sulphate the alumina, and re-dissolving the latter in caustic soda ley. Aluminate of soda is used in dyeing and calico-printing; further, for the preparation of lake colours, induration of stone, and the manufacture of artificial stone, and for the saponification of fats in stearine candle manufacture, an alumina soap being first formed, which is decomposed by acetic acid into acetate of alumina and free fatty acid. Aluminate of soda is largely used in the preparation of an opaque, milky-looking glass, or semi-porcelain. Aluminate of soda is a by-product of Balard's method of soda manufacture from bauxite, Glauber's salt, and coal; this by-product, or rather product of the second stage of the process, is decomposed by carbonic acid into carbonate of soda and alumina, which is thrown down. The Pennsylvania Salt Manufacturing Company at Natrona, near Pittsburg, manufacture large quantities of aluminate of soda, which is used in soap-boiling under the name of *natrona refined saponifier*.

Uses of Alum and of Sulphate of Alumina. Owing to the great affinity of the alumina contained in alum for textile fibres, especially wool and cotton, alum is largely used as a mordant in dyeing, except when the tar colours are employed. Again, owing to the affinity of alumina for many pigments, alum is employed in the preparation of the lake colours, combinations of active colouring principles with alumina. It is also used in the melting of tallow; for hardening gypsum; is found in the preparation used for sizing hand-made paper, the alum in this case forming with the glue or size an insoluble compound. Alum with resin is employed for the same purpose in machine-made paper, an alumina-pinate being formed. It is very largely used for the preparation of acetate of alumina, and with common salt in the tawing of leather. Alum is employed in clarifying turbid fluids, more especially water; in this case the alum takes up the alumina suspended in the water, and forming an insoluble (basic) alum carries down organic and other suspended impurities. A boiling solution of alum, common salt, and nitrate of potassa is used by jewellers for the purpose of colouring gold, that is to say, to produce a film of pure gold on the alloy, the copper of which is dissolved by the boiling solution.

Acetate of Alumina. This salt is prepared by double decomposition: generally sulphate of alumina and acetate of lead are used, and occasionally the acetates of baryta and lime. The liquor, separated by filtration from sulphate of lead, is gently evaporated to dryness; the dry salt is gelatinous, and does not crystallise, is very hygroscopic, and possesses a strongly astringent taste. When a solution of acetate of alumina is evaporated in contact with air, acetic acid is driven off, and a basic acetate, insoluble in water, formed. Commercially pure acetate of alumina is rarely used, as the so-called red-liquor, *mordant rouge*, consists of a mixture of alum, acetate of potassa, and sulphate of potassa. When it is desired to prepare neutral acetate of alumina from alum, to 100 parts of acetate of lead 62·6 parts of alum are required for complete mutual decomposition; but it is more advantageous to convert a solution of alum into insoluble alumina by means of carbonate of soda, and to treat with acetic acid. Acetate of alumina is not an ordinary article of commerce, as the salt is usually prepared by the consumers. Besides being largely used in dyeing and calico-printing, acetate of alumina is employed for waterproofing woollen fabrics. Among the salts of alumina employed industrially are—hyposulphite of alumina, suggested by E. Kopp as a mordant for cotton; hypochlorite of alumina, known as Wilson's bleaching-liquor, and used in bleaching-works; sulphite of alumina, for the purpose of purifying beet-root juice; oxalate of alumina, suggested by Dent and Brown for the preservation of stone, marble, dolomite, &c.

ULTRAMARINE.

Ultramarine. Native Ultramarine.

Under this name is now understood an artificial blue pigment, formerly and still obtained in small quantities from the *lapis lazuli*. The quantity of artificial ultramarine manufactured in Europe amounts to 180,000 cwts. annually. *Lapis lazuli* is a scarce mineral, possessing a beautiful blue colour. The sp. gr. varies from 2·75 to 2·95. The coarser pieces of this mineral are pulverised, heated to redness, and immediately dipped into water, then very finely ground, and the powder treated with dilute acetic acid to eliminate carbonate of lime. The powder is next well incorporated with a mixture of equal parts of resin, wax, linseed-oil, and Burgundy-pitch; this paste is kneaded under water until no more blue pigment remains suspended. The quantity of ultramarine obtained amounts to 2 to 3 per cent. This natural ultramarine is highly prized for its extreme beauty, softness of colour, and durability, not being affected by light, oil, and lime. Chemical analysis of the *lapis lazuli* first gave the clue to the true composition of this material, and led, after many unsuccessful attempts, to the preparation of artificial ultramarine, not, however, by any means equal to the native pigment, although it has driven smalt and other blue pigments nearly out of the market. *Lapis lazuli* consists in 100 parts of—silica, 45·40; alumina, 31·67; soda, 9·09; sulphuric acid, 5·89; sulphur, 0·95; lime, 3·52; iron, 0·86; chlorine, 0·42; and water, 0·12.

Artificial Ultramarine. Gmelin first made artificial ultramarine on a very small scale in 1822; but not before 1828 was ultramarine industrially obtained by Guimet, at Lyons. In Germany the first manufactories of ultramarine were established at Wermelskirchen, in 1836, by Dr. Leverkuss, and at Nuremberg, in 1838, by MM. Zeltner and Leykauf: the manufacture of artificial ultramarine in England is of very recent date, and is still on a very limited scale. France and Germany are the countries where this industry is most developed. Of late years the process of manufacture has been improved by R. Hoffmann, the manager of a factory at Marienberg, in Hessen; Wilkins, at Kaiserslautern; Fürstenau, at Coburg; and Gentele, at Stockholm.

Raw Materials. These are—1. Silicate of alumina as free as possible from iron, a good china clay, the kaolin of Cornwall being esteemed the best; 2. Calcined sulphate of soda; 3. Calined soda; 4. Sulphuret of sodium, as a by-product of the manufacture; 5. Sulphur; 6. Pulverised charcoal, or pit-coal.

Porcelain, or china-clay, is generally used, or a white clay, the composition of which is nearly the same. Small quantities of lime and magnesia have no injurious effect, but the oxide of iron should not exceed 1 per cent. The composition of the clay should approach as nearly as possible to the formula $Si_2O_7Al_2$; the silica may be combined or partly free. The clay is washed with water and treated in the same manner as for the making of porcelain; it is next dried, ignited, and ground to a very fine powder. The sulphate of soda should not contain any free acid, lead, or iron. If the sulphate does not possess the requisite qualities it is dissolved in water, milk of lime being added to neutralise the acid and to precipitate oxide of iron. The clear solution is left to crystallise; and the crystals are ignited in a reverberatory furnace and then pulverised by millwork. The clear solution is in some cases evaporated to dryness and ignited in iron vessels. Barium, but not potassium salts, form ultramarine (see "Chemical News," vol. xxiii., pp. 119, 142, 204). The calcined soda is obtained from the alkali works, and should contain at least 90 per cent. of carbonate of soda; it is also finely pulverised. Very recently caustic soda has been substituted in some ultramarine works. Sulphuret of sodium (Na_2S) is usually a by-product of the process of making ultramarine, and is obtained either in solution or as a dry powder. The sulphur is used very finely pulverised. The carbonaceous matter employed is also in a very fine powder. Its use was introduced by Laykauf for the purpose of deoxidation. In order to have the carbon in as finely divided state as possible it is ground to a pulp with water under granite stones; the pulp is lixiviated, and the fine powder obtained dried and passed through a sieve: in some cases resin and pitch is employed. For those ultramarines not to have their colour discharged by alum, pure silica, either as fine glass, sand, or pulverised quartz is used. Several substances are used to reduce the depth of colour of ultramarine, viz.—gypsum, sulphate of baryta, baryta-white, and flour; the last is employed in making up washing-blue.

Manufacture of Ultramarine. The methods of ultramarine preparation may be classified, according to the crude materials employed, as the three following:—

α. Preparation of Sulphate, or Glauber's salt ultramarine.
β. " " Soda-ultramarine.
γ. " " Silica-ultramarine.

α. *Preparation of Sulphate-Ultramarine.*—This ultramarine is prepared according to the Nuremberg process from kaolin, sulphate of soda, and charcoal; the preparation consisting in two distinct stages, viz.:—

a. Preparation of green ultramarine.
b. Conversion of green into blue ultramarine.

a. Preparation of Green Ultramarine.—In order to obtain a most intimate mixture of the dry and finely pulverised materials, small quantities are weighed off, mixed in wooden troughs by means of shovels, and several times passed through sieves. If solutions of Glauber's salt, soda, and sulphide of sodium are used instead of powders, the kaolin is mixed with these solutions, and the whole evaporated to dryness, gently ignited in a reverberatory furnace, and then pulverised and sifted. The quantities of the crude materials vary, but the following conditions have to be complied with:—1. Soda, whether sulphate or caustic, must be present in such quantity that it can saturate half of the silica of the clay (kaolin). 2. There must be sufficient soda remaining to form with the sulphur a certain quantity of polysulphuret of sodium. 3. There ought to remain enough sulphur and sodium to form another sodium sulphuret (Na_2S), after deducting from the whole mixture as much green ultramarine as, according to its composition as proved by recent analysis, the silica and alumina present are capable of forming. The following figures will give an idea of the proportions:—

	I.	II.
Kaolin (dried)	100	100
Calcined Glauber's salt ..	83—100	41
Calcined soda	—	41
Carbon (char- or pit-coal) ..	17	17
Sulphur	—	13

For 100 parts of calcined soda 80 parts of calcined Glauber's salt, and for 100 parts of the latter 60 of dry sulphuret of sodium are taken.

It is usual to have a large quantity of this mixture prepared for use. If this mixture is ignited without access of air, a white mass is obtained, which, having been treated with water, is a light, somewhat flocculent, white substance, to which Ritter has given the name of white ultramarine. It becomes green by exposure to air, and blue by being calcined in contact with air. The mixture is well rammed into fire-clay crucibles, placed in furnaces similar in construction to those used for burning porcelain, being raised and maintained at a high temperature with a very limited supply of air. This operation lasts seven to ten hours, and is completed at a bright white heat. The furnace is closed and slowly cooled; on removing the crucibles, the contents appear as a semi-fused grey- or yellow-green mass, which is repeatedly treated with water. The ultramarine thus obtained is in porous lumps, which are pulverised to an impalpable powder; this is washed, dried, and again ground, then sifted, and finally packed in boxes or casks, and sent into the market as green ultramarine, consisting, according to Stölzel's analysis (1855), in 100 parts, of—

Alumina	30·11	
Iron	0·49	(peroxide of iron, 0·7)
Calcium	0·45	
Sodium	19·09	(soda, 25·73)
Silica	37·46	
Sulphuric acid	0·76	
Sulphur	6·08	
Chlorine	0·37	
Magnesia, potassa, phosphoric acid	traces	
	94·81	
Oxygen	5·19	
	100·00	

Green ultramarine is a pigment of comparatively inferior value, owing to its being less brilliant than the green copper pigments.

b. Conversion of Green into Blue Ultramarine.—This operation may be variously effected, generally by roasting the green ultramarine and sulphur at a low temperature with access of air, so as to form sulphurous acid, while a portion of the sodium is oxidised into soluble sulphate and afterwards washed out; but the sulphur originally present in the green ultramarine remains combined with a smaller quantity of sodium. The roasting may be variously carried out, but very frequently the apparatus consists of a fixed iron cylinder similar to a gas-retort, provided with a stirring apparatus, by means of which the mixture of green ultramarine and sulphur (25 to 30 lbs. of the former to 1 lb. of sulphur) is submitted equally to the source of heat. The addition of sulphur is repeated until the desired blue colour is produced; but in some works this calcination is interrupted by repeated lixiviation, the object being to produce a superior article. Muffle-ovens and a kind of reverberatory oven are also used for this operation. The sulphurous acid, which is evolved in large quantities, is now generally employed in making sulphuric acid, sometimes a co-product of ultramarine manufacture, and used for the preparation of the sulphate of soda required. The ultramarine, when quite blue, is pulverised, lixiviated, dried, and finally separated into various qualities known in the trade as No. 00, 1, 2, 3, &c.

Preparation of Soda-Ultramarine.

β. As manufactured in France, Belgium, and some parts of Germany, this ultramarine is either pure soda-ultramarine or a mixture of soda- and sulphate-ultramarine. The materials and proportions are—

	I.	II.	III.
Kaolin	100	100	100
Sulphate	—	41	—
Soda	100	41	90
Carbon (charcoal or pit-coal)	12	17	6
Sulphur	60	13	100
Rosin	—	—	6

The ignition takes place either in crucibles, or, better, in a reverberatory furnace; the result is the formation of a brittle and porous green substance, which absorbs oxygen very rapidly, so that during the cooling of the mass in the oven, the greater part is converted into blue ultramarine. The complete conversion, after the addition of sulphur, is obtained by heating in a large muffle to redness, the product being distinguished from the foregoing by a greater depth and beauty of colour. By increasing, within certain limits, the quantities of soda and sulphur, the formation of blue ultramarine may be at once obtained, the product containing 10 to 12 per cent. of sulphur.

Preparation of Silica-Ultramarine. Silica-ultramarine is really soda-ultramarine in the preparation of which silica to the amount of 5 to 10 per cent. of the weight of the kaolin is added. The calcination at once yields blue ultramarine, and further treatment with sulphur is therefore unnecessary.

This ultramarine is not acted upon by a solution of alum, and may be recognised by its peculiar red hue, the intensity of which is increased by an increase of silica. Notwithstanding the superiority of the ultramarine obtained by this process, its preparation is disadvantageous owing to the tendency of the mixture of crude materials to fuse during ignition.

Constitution of Ultramarine. Since 1758 the chemical constitution of ultramarine has been the object of a series of researches. The latest experiments are those of W. Stein, who comes to the conclusion that ultramarine consists chiefly of a white mass, with which black sulphide of aluminium is most intimately and molecularly incorporated, the blue colour being due, not to chemical composition, but to the optical relation of its component substance. Green ultramarine contains less soda than the blue pigment, and that again less than the white (so-called) ultramarine. The quantity of sulphur contained in blue ultramarine is less than that in green.

Properties of Ultramarine. Artificial ultramarine is an impalpable powder of a fine blue colour, entirely insoluble in water, and when washed with distilled water leaving no residue on evaporation of the filtrate. It is not acted upon by alkalies, but is highly sensitive to the action of even very dilute acids and acid salts, sulphuretted hydrogen being evolved and the colour discharged. Native ultramarine obtained from *lapis lazuli* is not thus decomposed by weak acid solution. There sometimes accidentally occurs in soda furnaces a more or less blue ultramarine which exhibits the same resistance to acids. That kind of ultramarine commercially termed acid proof is manufactured with the addition of silica, as described, but it really only resists the action of alum-salts. Ultramarine is now largely used for the purposes to which smalt, litmus, and Berlin-blue were applied: that is to say, ultramarine is employed as a paint, as a pigment in stereochromy, for paper-hangings, calico-printing with albumen as fixing material, for colouring printing-ink, for the bluing of linen and cotton fabrics, paper, stearine, and paraffine-candles, and lump-sugar. For 1000 cwts. of sugar 2½ lbs. of the pigment are employed, a quantity so small as to be perfectly innocuous; further, ultramarine does not contain anything injurious to health. Green ultramarine is a dull-coloured powder used by wall-paper stainers, and is sometimes mixed with indigo-carmine and a yellow pigment to improve the colour.

Adulterations of ultramarine with Berlin-blue, smalt, and other blue pigments do not now occur, as ultramarine is a cheaper material; but to obtain lighter tints ultramarine is sometimes mixed with chalk, kaolin, alabaster, and chiefly with sulphate of baryta.

DIVISION III.

TECHNOLOGY OF GLASS, CERAMIC WARE, GYPSUM, LIME, AND MORTAR.

Glass Manufacture.

Definition and General Properties of Glass. Glass is an amorphous composition of various silicates obtained by a process of smelting, alkaline and calcium silicates being the chief constituents. That which is termed glass-water—viz., a silicate of potassa or soda—of course contains no other silicates; but real glass contains other bases in addition to soda and potassa, either alkaline earths, as lime, baryta, strontia, or other more or less basic bodies, as magnesia, alumina, or metallic oxides,—those of lead, bismuth, zinc, thallium, protoxides of iron and manganese, while in the case of optical or fine crystal glass boracic acid or borax is substituted for a portion of the silica.

Glass is generally transparent; when opaque it is either white or coloured. Glass is not acted upon, in the common acceptance of the term, by either water, acids, or alkalies. It is, as has been said, amorphous, for as soon as it becomes crystalline it ceases to be glass. The amorphism of glass is due to its composition; simple silicates have a tendency to crystallise, and are hence unfit for glass manufacture. Owing to its amorphism glass exhibits a conchoidal fracture. When blown to very thin laminæ or drawn into thread, glass possesses a remakable degree of elasticity. As regards the chemical and physical qualities of glass, much depends upon the constituent silicates; the alkaline silicates render glass soft and contribute to its ready fusibility. Silicate of potassa glass is less bright and glossy than glass in which silicate of soda prevails, but the latter silicate imparts a blue-green colour. Silicate of calcium renders glass harder, brighter, but less readily fusible. Silicates of lead and bismuth render glass very fusible, impart to it a high degree of lustre, and greatly increase the refrangibility; they are therefore used in making glass for optical purposes. Silicates of zinc and baryta impart similar properties; the former has the property of reducing the blue-green colour due to silicate of soda. Silicates of iron and manganese render glass readily fusible, and impart colour to it. Silicates of other metallic oxides are only of secondary importance in imparting colour to glass.

Classification of the Various Kinds of Glass. According to its chemical composition glass may be classified as follows:—

I. Potassium-calcium glass, or Bohemian crystal glass, is quite colourless, very difficultly fusible, hard, and very difficultly acted upon by chemicals. Abroad, mirrors are often made of this glass, mixed with any of the following kinds.

II. Sodium-calcium glass, French glass, window glass, somewhat harder than the preceding but more readily fusible, exhibiting, as does all soda-containing glass, a peculiar blue-green hue. Crown-glass is of similar composition.

III. Potassium-lead glass, crystal glass, very readily fusible, soft to cut, has a higher sp. gr. than other glass, and is more refractive. Among the varieties of this glass are:—1. Flint-glass, optical glass, in addition to lead often containing bismuth and boracic acid. 2. Strass used for preparing imitation gems.

IV. Aluminium-calcium-alkali glass, or bottle-glass, always contains oxides of iron and manganese; and sometimes magnesium instead of calcium. The colour varies from a red-yellow to a deep black-green.

The sp. gr. of glass depends upon its composition. The alkali-calcium glass is the lightest, next follows aluminium-calcium-alkali glass, while thallium glass is the heaviest, as may be seen in the following table:—

Bohemian crystal glass	2·396	Sp. gr.
Crown-glass	2·487	,,
Mirror-glass	2·488	,,
Window-glass	2·642	,,
Bottle-glass	2·732	,,
Lead glass	2·9 to 3·255	,,
Flint-glass (Fraunhofer's recipe)	3·77	,,
,, (Faraday's ,,)	5·44	,,
Thallium glass	5·62	,,

Slowly cooled glass possesses single, rapidly cooled doubly refractive powers; the refractive index of glass differs considerably, but is never so high as that of the diamond. Taking the index of refraction of the vacuum of Torricelli as unity, that of quartz is = 1·547; diamond, 2·506; optical glass (2·52 sp. gr.) = 1·534 to 1·544; flint-glass of 3·7 sp. gr., 1·639; thallium glass = 1·71 to 1·965.

Raw Materials used in Glass-making. These are:—1. Silica, viz. quartz, for very pure glass, for other kinds sand of varying quality or pulverised flint stones. For very pure glass the silica ought to be free, or very nearly so, from iron; in some cases the peroxide of iron adhering to the quartz or mixed with the sand is removed by hydrochloric acid, while the sand is always first ignited and in some instances previously washed to remove clay, marl, humus, &c. Ordinary glass is made with coarser materials, the sand is not required to be so pure, as when it contains lime, chalk, or clay, it renders the mass more fusible.

2. Boracic acid is sometimes used as a substitute for a portion of the silica. It increases the fusibility of the glass, imparts to it a high polish, and prevents devitrification. It is employed as borax or as a boro-calcite, a native boracic acid.

3. Potassa and soda are used in a variety of forms, the former chiefly as potash (carbonate of potassa), or partly lixiviated wood-ash.

Not so large a quantity of soda is required as of potash; 10 parts of carbonate of soda correspond to 13 parts of carbonate of potash. Recently the soda has been used in the form of Glauber's salt; in this case, so much carbon is added to the siliceous earth and Glauber's salt as will reduce the sulphuric acid of the sulphate of soda to sulphurous acid, and the carbon to carbonic oxide. The silicic acid then easily decomposes the sulphurous acid of the sulphite. To 100 parts of Glauber's salt (anhydrous) 8 to 9 parts of coal are measured. An excess of carbon is detrimental, as a large quantity of sulphide of sodium is formed, which imparts a brown tint to the glass.

4. The lime used in glass-manufacture must be free from iron. It is generally employed as marble or chalk, either raw or burnt. To 100 parts by weight of sand, 20 parts by weight of lime are added. In the Bohemian manufacture the lime is employed as neutral silicate of calcium, Wollastonite, SiO_3Ca. Instead of lime, strontia, and baryta can be used, the former as strontianite ($SrCO_3$), the latter as witherite ($BaCO_3$). Fluor-spar ($CaFl_2$), and aluminate of soda were at one time used in making milky or semi-opaque glass.

5. Oxide of lead is employed in most cases in the form of minium or peroxide, giving up some of its oxygen to form a lower oxide, and purifying the glass. The lead gives the glass a higher specific gravity, greater brittleness, transparency, and polish. It must be

free from oxide of copper and tin, the former imparting a green colour, and the latter an opacity to the glass. White-lead is as efficacious as red-lead, provided no heavy spar be present.

6. Oxide of zinc is always added as zinc-white. When the colour is not of importance, zinc-blende with sand and Glauber's salts may be used.

7. Oxide of bismuth is only added in small quantities in the preparation of glass for optical instruments. Bismuth may be employed either as oxide or nitrate of the oxide.

The natural silicates are only employed alone in the manufacture of bottle-glass; some of the preceding additions are requisite in clear glass manufacture.

Bleaching. Coloured glass as it occurs in the first process of manufacture may have the colour disguised by mechanical mixture with white glass, or the colour may be discharged by chemical agents. Such agents are usually—braunite, arsenious acid, saltpetre, and minium or red-lead.

1. Braunite, MnO_2, has long been used as a material for glass-clearing. This oxide of manganese is, however, used only in small quantities; too much imparts a violet or amethyst-red colour to the glass; while an excessive amount renders the glass dark coloured and opaque. The violet-coloured glass is generally prepared with silicate of manganese by the addition of braunite to colourless glass. The action of braunite in clearing glass or rendering it colourless has been variously explained. It may be considered that there arises in the molten glass the colours complementary to white, that is, the green from silicate of iron and the violet from silicate of oxide of manganese; this view is supported by the experiments of Korner, who obtained a colourless glass from a mixture of red and violet glasses; and further by those of Luckow who obtained a colourless glass by the melting together of a glass strongly tinted red by protoxide of manganese with oxide of copper. The glass-blowers of the Bavarian Waldenses assert that a rose-red quartz there found is equalled by no other quartz in the production of the best crystal or clear glass. Von Fuchs says that this quartz contains 1 to 1·5 per cent. of oxide of titanium, which similarly to braunite, effects the chromatic neutralisation. Kohn employs for this purpose protoxide of nickel or oxide of antimony. Oxide of zinc has lately been employed to remove or mask the green colour of Glauber's salt glass, also imparting a higher polish. 2. Arsenious acid effects the removal of colour by chemical means only from glass containing carbon or silicate of iron: in glass containing carbon—

$$\left.\begin{array}{l}\text{Arsenious acid, } As_2O_3\\ \text{Carbon, } 3C\end{array}\right\}\text{give}\left\{\begin{array}{l}\text{Arsenic, } As_2,\\ \text{Carbonic oxide. } 3CO\,;\end{array}\right.$$

in glass containing protoxide of iron:—

$$\left.\begin{array}{l}\text{Protoxide of iron, } 6FeO,\\ \text{Arsenious acid, } As_2O_3,\end{array}\right\}\text{give}\left\{\begin{array}{l}\text{Oxide of iron, } 3Fe_2O_3,\\ \text{Arsenic, } As_2.\end{array}\right.$$

The arsenious acid is reduced by the carbon and protoxide of iron at a dull red heat, while the arsenic is volatilised.

3. Saltpetre is added chiefly as Chili-saltpetre or nitrate of soda. In the manufacture of lead-glass (flint-glass) nitrate of lead is substituted for the nitrate of soda. Nitrate of barium has recently been employed to discharge the colour of glass; its action is similar to that of arsenious acid.

4. That minium serves to render glass colourless has already been noted. Chambland states that glass may be whitened by forcing through it while molten a stream of air.

Utilisation of Refuse Glass. The materials of glass manufacture are never melted alone, but always with nearly the third part of prepared or finished glass. For this purpose, pieces of broken glass, flaw glass, the hearth droppings, and the glass remaining adherent to the blowers' pipes may be utilised,—serving a purpose in the manufacture of glass similar to the rags in paper-making. Thus there is only a very small loss of materials. At each re-melting, however, a portion of the alkali of the fragmentary glass is volatilised, and must be replaced by the addition of an alkaline salt.

The Melting Vessel. The vessels in which the glass is melted are placed immediately upon the hearth, and are made of difficulty-fusible clay and powdered chamotte-stone. They are usually 0·6 metre in height, the walls being 9 to 12 centimetres thick. They are dried in a temperature of 12° to 15°, and then placed in a chamber heated to 30° to 40°. After remaining about a month, the vessel is put into the tempering or annealing oven, heated to 50°; it is next removed to the ordinary melting-oven, and gradually heated to the melting-point of glass, at which it remains for three to four hours. When a new pot is first used for glass-melting, the alkaline constituents of the glass act upon the clay, forming a rich clay glaze or glass, which, if allowed to mix with the ordinary glass, would be highly detrimental. Consequently broken glass and refuse are first melted in the vessel, and the glaze imparted, termed technically the lining, is a sufficient protection to the glass in after practice. The shape of the melting vessels varies. For melting with wood or gas the conical form, Fig. 120, is employed. When coal is used as fuel, the vessel takes the covered form, Fig. 121. Fig. 122 represents a rather peculiar form; the glass constituents are melted in A, the clear molten glass passing by the aperture in the central wall into B. The glass in B is thus always free from glass-gall or impurities, which remain behind in A. In the manufacture of looking-glasses, large quadrangular vessels, Fig. 123, are employed for refining purposes.

FIG. 120.

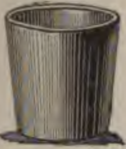


FIG. 121.

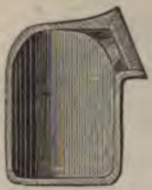


FIG. 122.

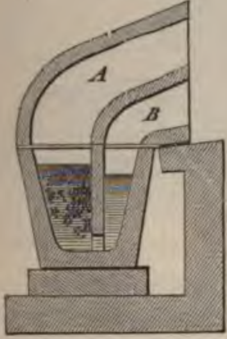
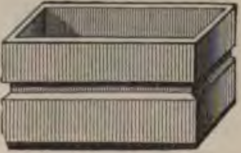


FIG. 123.



The Glass-Oven. The glass-ovens are respectively—1. The melting-oven; 2. The tempering- or annealing-ovens, used in the after-manufacture. The melting-oven can only be made of fire-proof clay. It is built of a mixture of white clay and burnt clay of the same kind. Ordinary mortar and cements are useless for this purpose on account of their fusibility, therefore the same clay as is used for building is also used for binding. The oven must be built on dry ground; if built on damp ground it is difficult to maintain the lower parts at a constant heat, requiring a larger supply of fuel. The arch is closed with a single piece of fire-proof clay weighing 800 to 1000 cwts. After building the oven is dried for four to six months at a temperature of 12° to 15°; a low fire is then lighted, and the temperature gradually increased for about a month until the oven is fit for actual work. The arch is further covered with massive backstones, and these again are covered to a thickness of 5 to 6 inches with a lime-mortar. When much in use, and if not built of very good clay, an oven will not remain in working order for longer than $1\frac{1}{4}$ to $1\frac{3}{4}$ years; but if fire-clay is used, and only easily-fusible lead-glass is manufactured, the oven may last for four to five years. The oven contains six or eight to ten melting-pots, which must all be raised to the same temperature. Further, the melting-oven is placed over half the fire-room. The annexed woodcut, Fig. 124, is a ground plan of a complete oven. Fig. 125 is a section showing the melting-oven and work-holes; Fig. 126 a vertical section through the length of the oven; Fig. 127 a vertical section of the breadth. In the ground plan, Fig. 124, *o o* is the flue; *c c c* are the melting-pots; *n n*, pots containing glass in another stage of preparation; *d d d*, the work-holes; *b b*, the banks; *i i*, warming and cooling ovens; *h h*, tempering ovens; *e e*, the breast walls; *f f*, the splint walls; *l l* are small hearths to increase the heat in the tempering oven when required.

FIG. 124.

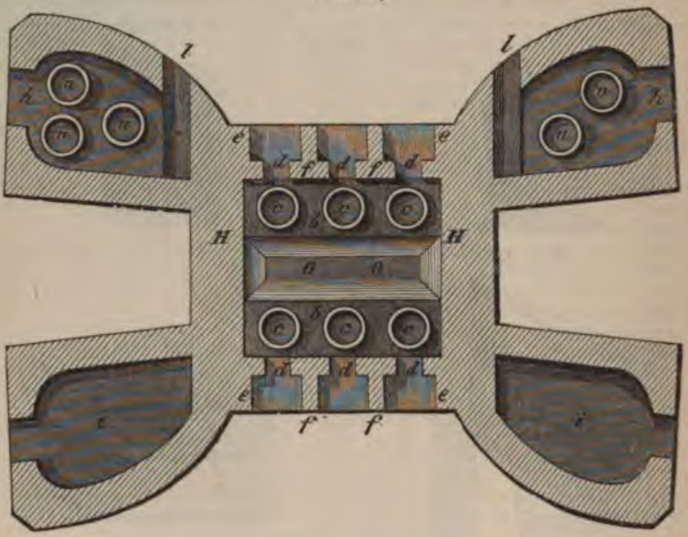
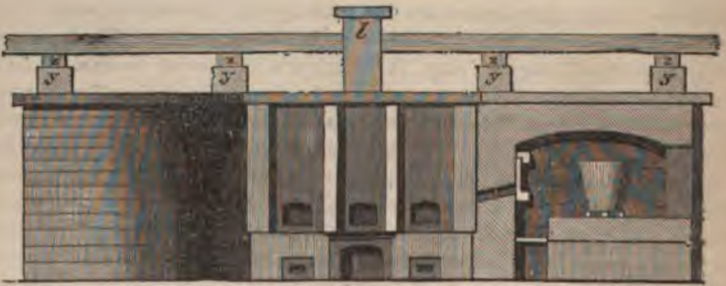


FIG. 125



In Fig. 125 *l* is the flue; *y y* are blocks of stone, bearing the wooden frame-work, *z z*, on which the wood used as fuel is placed to dry. Fig. 126 shows the bank, *f f*, on which the melting-pots, *h h h*, stand; over these pots are the work-holes; *n n* are the side chambers. In Fig. 127, *b b* is the key-stone; *c d* are the banks; *g* the flue, although in most glass-ovens there are no flues. The flame from the fuel burning in both grates, *m m*, Fig. 126, after heating the melting oven, passes by the tempering rooms, and finally to the chimney-stalk.

Siemen's gas-oven has lately found extensive use. At the Paris International Exhibition of 1867 this oven obtained the gold medal. It consists of two parts, the generator, Fig. 128, and the melting oven, Fig. 129. These parts are separate, and can be 30 or more metres from each other, being connected by a large gas-pipe. The fuel, brown coal, turf, stone coal, or wood, is placed in the generator at A, Fig. 128, and falls on the sloping grid, O. The gas, a mixture of carbonic oxide and nitrogen, ascends at a temperature of 150° to 200°, and flows out of the generator by a large pipe, V, 4 to 5 metres in height, and is conveyed thence by a horizontal pipe to the

Fig. 126.

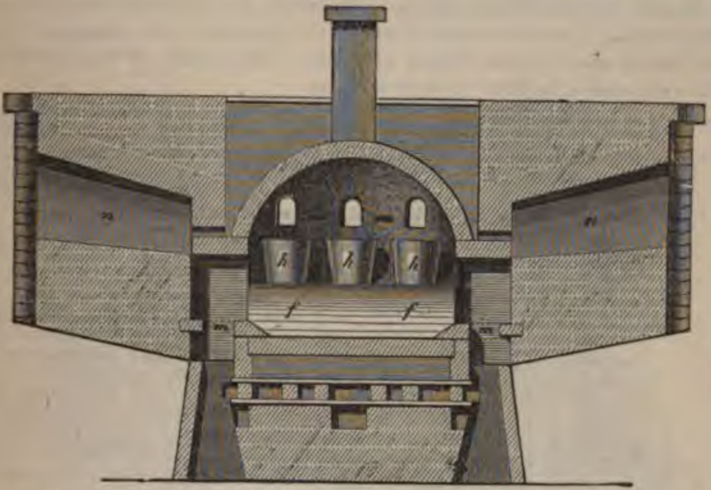
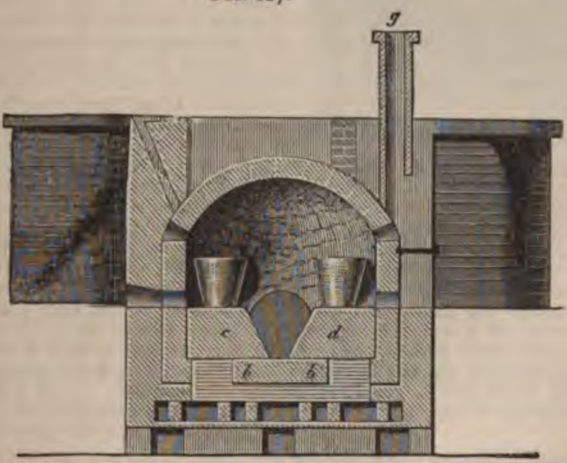


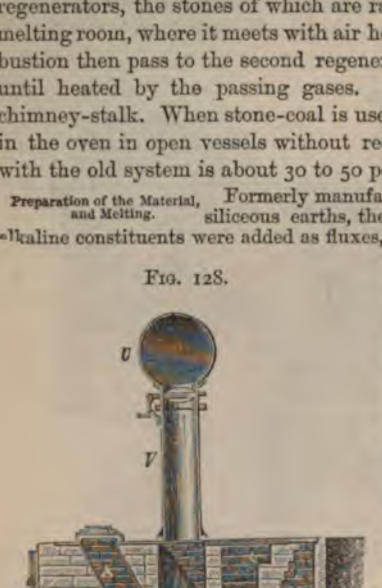
Fig. 127.



melting oven. The upper chambers of the melting oven are similar to those of the usual ovens. P P are the melting-pots. The gas first passes into the first system of regenerators, the stones of which are raised to a red-heat, and passes thence to the melting room, where it meets with air heated in like manner. The products of combustion then pass to the second regenerating system, the stones of which are cold until heated by the passing gases. The waste gas is finally conducted to the chimney-stalk. When stone-coal is used in the generator, lead-glass may be melted in the oven in open vessels without reduction. The saving of fuel in comparison with the old system is about 30 to 50 per cent.

Preparation of the Material, and Melting. Formerly manufactured glass was only an imitation of crystalline siliceous earths, the chemical action being but little known. The alkaline constituents were added as fluxes, and to this day retain that name. However, most of the results attending the variations of temperature were known, and, in fact, the chief practical detail.

Fig. 128.

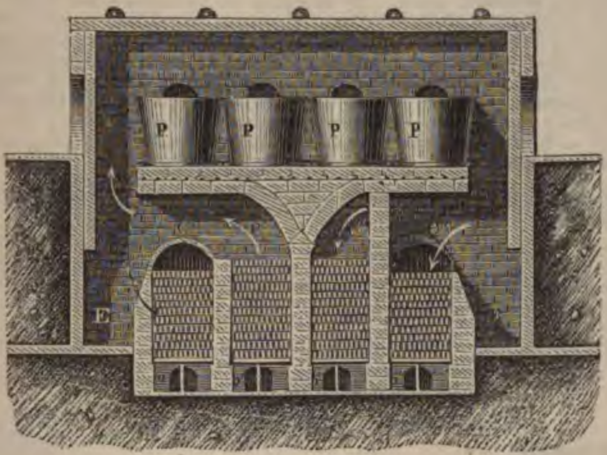


Of especial importance in glass manufacture is the knowledge of the behaviour of glass in the fire. At the maximum temperature of glass-melting ovens, 1200° to 1250° C., the glass forms a thin fluid of the consistency of syrup. This condition is essential to the refining of the glass, as the thinness of the fluid admits of the settlement of foreign substances to the bottom, or of their floating to the surface of the glass contained in the melting-pot. In this condition also the clear molten glass can be run off. At a red-heat glass is exceedingly ductile and flexible; upon this quality depends its application in manufacture. Two pieces of glass raised to a red heat can be welded into one piece by mere pressure. Glass as a fine thread is generally flexible, and may be spun. Undoubtedly glass will be used as a spinning-fibre at some future time; even now, in the International Exhibition of 1871, there are several articles of habiliment made of spun glass, exhibited by an Austrian firm. Brunfaut, of Vienna, in 1869, prepared glass-wadding, feathers, bows, favours, nets, &c. Glass fibre, according to the measurement of Fr. Kick, of Prague, can be spun to a diameter of 0·006 and 0·012 millimetres. When glass is allowed to cool extremely slowly it loses its transparency, and is transformed into an opaque mass known as Réaumur's porcelain. The chemical action taking place when glass is rendered opaque is, in spite of numerous researches, still unexplained. On the other hand, glass cooled too suddenly acquires peculiar properties. Detonating bulbs are small glass flasks which have been cooled immediately after being made. If a sharp grain of sand be dropped into the interior of one of these flasks it will fly to pieces with excessive violence, while the exterior will bear hard usage without result. Another peculiarity of glass manufacture are glass-tears, or Prince Rupert's drops, long pear-shaped drops of glass, tapering to a very slender tail, which are formed by dropping molten glass into cold water. The bulb of these drops may be struck with a hammer; but if only a small portion of the tail be snapped off, the entire drop will break up with a loud report. This brittleness is more or less the characteristic of all unannealed glass, and is probably due to unequally cooled layers, which are consequently at different degrees of tension.

Drying the Materials. Before the materials are placed in the melting oven, they are first subjected to a tolerably strong heat, not sufficient, however, to effect fusion in the drying oven. The benefit of this operation is the removal of the carbonic acid and water which would otherwise be disseminated in the melting oven. Some manufacturers dispense with this portion of the process, running a risk of turning out imperfect glass that can be avoided at a very small expense.

Melting the Glass Material. When the temperature of the melting oven has reached the required degree, the material first frits together and is then melted. The oven must be heated equably throughout. At the melting-point the siliceous earth combines with the potash, soda, lime, alumina, oxide of lead, &c., to form glass. The substances not taken up form a scum, known as glass-gall, upon the molten glass, which is removed by the aid of iron shovels. This scum is generally composed of sulphate of soda and chlorides of the alkalies. The progress of the melting process is from time to time ascertained by removing a sample of the glass by the help of an iron rod terminating in a flat disc, in fact a large flat spoon.

FIG. 129.



Clear-melting. When the mass is well molten it is "cleared," that is, maintained for some time at such a temperature that the glass remains in a thinly fluid condition. During this period the uncombined substances settle to the bottom of the melting vessel, the air-bubbles disappear, and the glass-gall still remaining is volatilised or separated. At the commencement of the melting the disengagement of the gases from the molten mass causes an advantageous agitation, by which the several constituents of unequal specific weight and different composition become well mixed. After the disengagement of the gases the lower part of the melting vessel is at a lower temperature than the upper part, consequently the molten glass is well stirred with the iron ladles or "poles." Lastly, a piece of either arsenious acid, damp wood, raw turnip, or any other water-containing substance, is introduced to the bottom of the vessel on an iron rod, the end in view being the violent agitation of the molten glass by the steam evolved.

Cold-stoking. After the completion of the clearing follows the cold-stoking, that is, the lowering the temperature of the oven till the glass attains a tough fluid consistency requisite before it can be blown. The glass remains at this temperature, 700° to 800° C., during the rest of the manufacture.

The length of the several processes is as follows :—

Melting	10 to 12 hours.
Clearing	4 to 6 ,,
Blowing	10 to 12 ,,

so that five to six meltings can be effected in a week.

Defects in Glass. It is extremely difficult to prepare glass perfectly free from blemish. The principal defects are—streaking, threading, running unequally, or dropping, stoning, blistering, and knotting. Streaking follows from heating the glass unequally, another consequence of which is the threading or the formation of the striæ, by glazing, into coloured threads, generally green. By dropping is understood the lumps or globules formed in the glass by the glazing of the clay cover of the melting vessel, and its combination with the volatilized alkalies, the crude glass thus formed on the cover dropping into the molten glass contained in the vessel. Blistering is a common result of the imperfect clearing of the glass from air bubbles. Lastly, knotting, another common defect, results from uncombined grains of sand taken up in the glass; the small particles of the oven and melting vessel detached during the melting similarly giving rise to stoning. Other defects, such as the imperfect combination of the materials, arising from carelessness or inability of the workman, need not here be noticed.

Various Kinds of Glass. Glass is separated according to its composition or method of manufacture into :—

I. *Glass free from Lead.*

A. Plate-glass. *a.* Window-glass :—
  - *α.* Rolled glass.
  - *β.* Crown glass.

  b. Plate-glass :—
  - *α.* Blown plate-glass.
  - *β.* Cast plate-glass.

B. Bottle glass :—
  - *a.* Ordinary bottle glass.
  - *b.* Medicine and perfumery glass.
  - *c.* Glass for goblets, drinking glasses, &c.
  - *d.* Water pipes and gas tubes.
  - *e.* Retort glass.

C. Pressed or stamped glass.

D. Water glass.

II. *Glass containing Lead* (*Flint-Glass*).

A. Crystal glass.
B. Glass for optical purposes.
C. Enamel.
D. Strass.

III. *Coloured Glass and Glass Staining.*

IV. *Glass Decorations.*

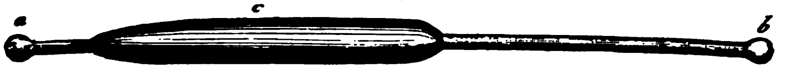
Plate or Window-Glass. The glass melted in muffles or vessels is manufactured as plate-glass or as crown-glass. Plate-glass, as its name implies, is formed in large or small plates; window glass is generally either ordinary bottle glass, or a finer glass of a whiter colour. Recently, thick has taken the place of thin glass for windows, but the colour is hereby considerably increased. That window glass should be prepared cheaply is an essential point, consequently crude materials are employed—crude potash and soda, wood-ash, Glauber's salt, ordinary sand, and broken glass from the warehouses, &c. Plate- or window-glass is generally composed of 100 parts sand, 30 to 40 parts of crude calcined soda, 30 to 40 parts of carbonate of calcium. Instead of the soda may be substituted an equivalent quantity of Glauber's salt. Benrath (1869) found in several kinds of plate-glass the following constituents:—

Silicic acid	70·71	71·56	73·11
Soda	13·35	12·97	13·00
Lime	13·58	13·27	13·24
Alumina and oxide of iron	1·92	1·29	0·83
	99·46	99·09	100·18

Tools. The tools ordinarily used by the glassblower in the preparation of plate- and crown-glass are the following:—

a. The pipe or blow-tube, Fig. 130, is an iron pipe 1·5 to 1·8 metres in length, 3 to 4 centimetres thick, and 1 centimetre interior diameter. *a* is the mouthpiece, made so as to turn easily between the lips. *c* is a hollow handle from 0·3 to 0·5 metre in length. *b* is the part attached to the glass.

FIG. 130.



b. The handle or hand irons are rods 1 to 1·3 metres in length, used to transport the hot vessels, &c. *c.* The marbel, Figs. 131 and 132, is a piece of wood with semi-globular indentations, which serve as matrices for the glass to be taken up on the blower's pipe. *d.* The whip, a block of wood, hollowed so as to form a long neck to the soft semi-molten glass; it is also used to remove the glass from the pipe. *e.* Fig. 134 are the shears used for trimming the molten glass, and to cut openings during the blowing of various articles.

FIG. 131.

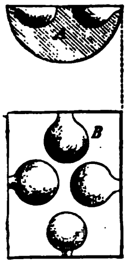


FIG. 132.

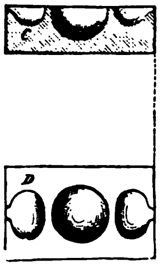


FIG. 133.

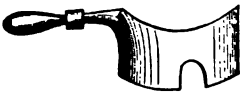
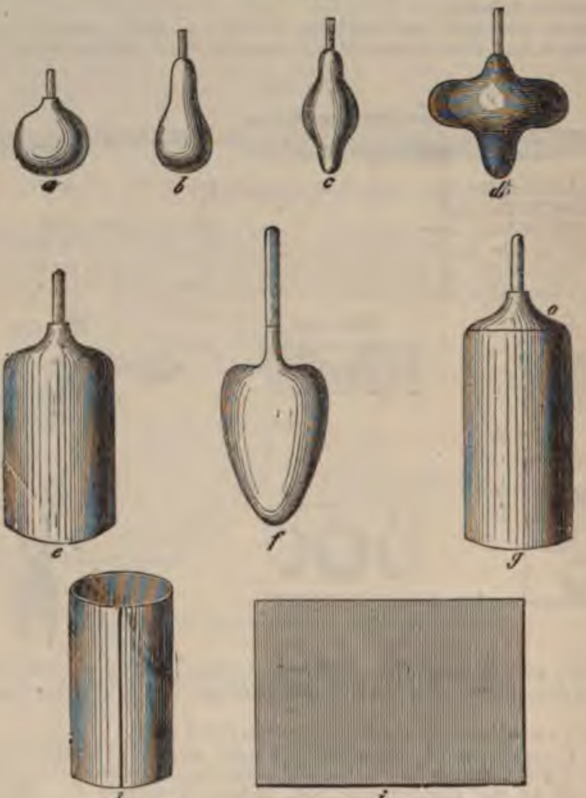


FIG. 134.

Plate-glass is manufactured as crown-glass or as rolled glass.

Crown-glass. Crown-glass is the oldest kind of window glass. It is formed in the manufacture as a disc of glass, generally of about six inches in radius from the periphery to the centre knot left by the glassblower's pipe, technically termed the bull's-eye. The largest discs are scarcely 64 to 66 inches, from which a square plate of 22 inches only can be cut, the bull's-eye interfering with the cutting of a larger size. In the preparation of this glass three workmen are employed; the first takes so much molten glass on the end of a pipe as will serve for a single disc, and passes pipe and glass to the second workman, the blower. He blows the glass into a large globe or ball, which, when finished, he hands to a third workman, the finisher, who opens the globe and forms the sheet or pane. The labour is divided in detail in the following manner:—The first workman receives the warm pipe, thrusts it into the vessel of molten glass, and turns it steadily round until he has collected upon the end a knob of glass of sufficient size. The weight of this knob is generally 10 to 14 lbs. The first workman imparts somewhat of a spherical form by means of the marbel to the solid glass ball, which is now taken in hand by the blower, who by turning and shifting the glass about, at the same time blowing through the tube, perfects the hollow spheroid. The glass has by this time cooled considerably, and with the pipe is therefore returned to the oven, the tube of the pipe being fastened in a fork or hook in the ceiling of the oven. As the globe of glass is gradually heated the weight of the rod causes it to flatten out, and it is removed by the finisher as a disc of nearly molten glass. He places the tube in the cavity of the whip, and by a series of dexterous movements perfects the shape, enlarges the disc if required, or in some cases makes a larger disc by removing the partially flattened sphere from the oven, opening the bottom with a maul or iron rod, and causing the glass to take the form of a disc by means of the centrifugal force resulting from a rapid rotary motion of the rod. Finally the discs are separated from the pipe by the help of a drop of cold water, and are next placed in an annealing oven to the number of 150 to 200 to cool. The finished plates are cut to the required size; the centres or bull's eyes serve for the making of strass and for other purposes.

FIG. 135.



Sheet Glass, or Cylinder Glass. Rolled or sheet glass is made by cutting a glass cylinder or roll throughout its length, and beating or rolling it out flat on a table. It is for this reason termed sheet glass. Usually this sheet glass is used for ground glass, and is further separated into ordinary sheet or roll-glass and fine sheet glass, the latter having larger dimensions.

The preparation of sheet glass is one of the most difficult processes of glass manufacture; it may be considered as consisting of two operations—

1. The blowing of the roll, or cylinder; and
2. The flattening.

After the molten glass has cleared, and attained the barely fluid consistency before mentioned, the workman inserts his pipe into the mass, and by turning manages to accumulate on it a globe of glass, during the time blowing into the tube to keep it clear of the molten glass. The glass now takes the form *a*, Fig. 135. By continued manipulation in the marbel, and by blowing, the enlarged forms, *b* and *c*, and finally *d*, are obtained. The glass has by this time cooled, and is taken to the oven to be re-heated. When this is effected, the workman by means of his tools, by a continued rotation of glass, and by blowing, brings the globe to the shape represented by *f*. He then opens out the bottom of this form with a maul-stick, and obtains the cylinder *e*, which is separated from the pipe by dropping a little cold water upon the neck, *o*, joining the two. The removal of this neck is next effected by means of a red-hot iron rod, which also serves to open the cylinder throughout its length as shown by *h*.

Fig. 136.

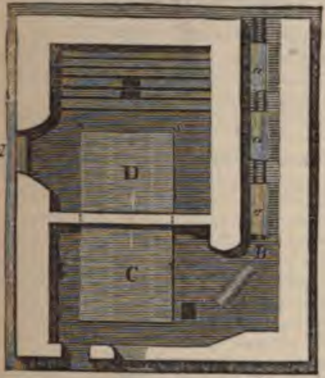
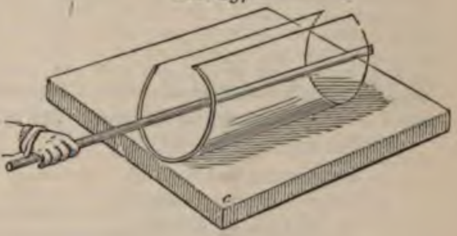


Fig. 137.



After a great number of these cylinders have been blown, the operation being generally continued for three days, the opening into plates is commenced. The cylinders are placed in an oven termed the plate-oven, shown in ground plan in Fig. 136, consisting of two chambers, one the heating room, C, and the other the tempering or annealing room, D. In the passage B, the heated glass rolls or cylinders, *a a a*, are suspended upon two iron rods, where they are maintained at a certain heat. The most important part of the plate-oven is the platten, C, made of a well-rammed fire-clay. A similar plate, D, is placed in the annealing room. When sufficiently heated, the cylinders are brought to the flattening table, *c*, Fig. 137, where they are speedily opened out in the manner shown in the woodcut. A workman stationed at *d*, Fig. 136, receives the flat panes of glass, and leans them against the iron bars, *s s*, in the annealing room, whence, having gradually cooled during four to five days, they are removed to be sorted and packed.

Plate-Glass. Plate-glass is either blown or cast. The manufacture is very similar to that of table-glass just described. The materials are in great part the same as those employed in the manufacture of fine white glass. This branch of glass manufacture is most strikingly illustrative of the rapid growth of the industry during the last ten or twenty years. Formerly plate-glass was esteemed an article of luxury, whereas now it is that most generally used for workshop windows, carriages, show-rooms, &c., and for windows of private residences. It far surpasses in transparency and elegance the small panes formerly used. By the Glass Jury of the International Exhibition of Paris of 1867, it was surmised that before ten years had elapsed plate-glass would be that most generally in the market. The blowing of plate-glass is effected with the same tools as the blowing of table-glass; and the cylinder is obtained in a similar manner. The lump of glass taken by the blower on his pipe from the melting vessel weighs about 45 lbs., from which a plate of 1·5 metres in length and 1 to 1·1 metres breath by 1 to 1·1 centimetres thickness is obtained. But the chief method of making plate-glass is by casting. Cast plate-glass is always made from pure materials, and may be considered as a soda-calcium glass free from lead. Potash-calcium glass is far more expensive, being almost a colourless glass. In England, Belgium, and Germany the raw materials used in manfacturing cast plate-glass are—sand, limestone, and soda, or Glauber's salts.

Benrath (1869) found in English (α) and in German (β) plate-glass:—

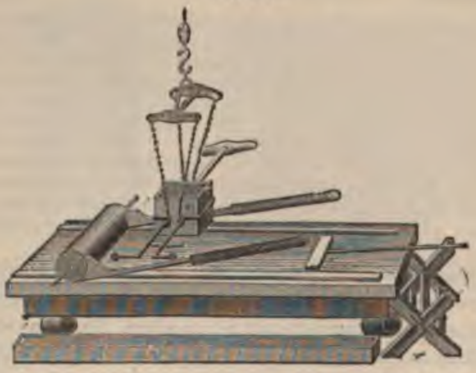
	α.	β.
Silica	76·300	78·750
Soda	16·550	13·000
Lime	6·500	6·500
Alumina and oxide of iron	0·650	1·750
	100·000	100·000
Sp. gr.	2·448	2·456

The following description of casting the plates is mainly founded upon the method pursued at St. Gobin and Ravenhead. The manufacture is included in—

1. The melting and clearing,
2. The casting and cooling,
3. The polishing: including
    - α. The rough-polishing,
    - β. The fine-polishing,
    - γ. Finishing.

The Melting and Clearing. The melting and clearing vessels are of very different form and size. The first is a conical vessel surmounted by a cupola having three apertures, making an angle of 120° with each other. The clearing pans are small, wide, and low vessels. These vessels are never in the same oven. After the materials are melted, which is effected in sixteen to eighteen hours, the molten mass is poured into the clearing vessels.

Fig. 138.



Casting and Cooling.

The impurities are then removed with a large copper ladle, this process occupying about six hours. During the clearing the excess of soda is volatilised. When the glass is sufficiently cleared the casting commences. The vessel containing the molten glass is taken up by a crane and swung to the casting table, this table or mould being on a level with the cooling or annealing oven. The casting table consists of a large polished metal plate, Fig. 138, in the French work of copper or bronze, 4 metres long, 2·25 metres wide, and 12 to 18 centimetres thick. The plate at St. Gobin weighs 55,000 lbs., and cost 100,000 francs (£4000). In England the plates are of cast-iron, 25 centims. thick, 5 metres in length, and 2·8 metres wide. In order that the glass plate shall be of equal thickness, a bronze or cast-iron roller passes over the surface on guides of the thickness required. The metal plate is first warmed to prevent the sudden cooling of the glass. The operation of casting includes—

a. The conveyance of the pan to the table;
b. The cleansing of the plate and the pan;
c. The casting and conveyance of the plate to the annealing room.

The cooling room has two fire-places and three glass tables. The temperature is at first that of the glass plate introduced. So soon as three plates are placed in the oven, all the openings are closed, and the glass left for a day to cool. The cooled glass plate is taken out of the annealing oven to the cutting room, laid on a cloth-covered table, and cut to size with a diamond.

Polishing. The glass plate is cut into tablets. The under side of the plate, where it has been in contact with the table, is smooth, while the upper surface is wavy, and requires to be polished. This is effected by fastening the plate or tablet to a bench with plaster-of-Paris, and grinding the upper surface smooth with some sharp powder; or another plate is caused by machinery to move above the former in such a manner that the surfaces of both are ground smooth. The ground plates are then removed to the polishing table, where a similar process is gone through, but with a finer powder. Finally, when placed upon the finishing table only the finest powder and leathern pads are employed. By grinding and polishing the glass sometimes loses half its weight and thickness. Suppose a plate-glass manufactory to produce 400,000 square feet of glass annually, there will be with this amount of glass weighing about 16,000 cwts., a loss of 8000 cwts., corresponding to 2700 cwts. of calcined soda, and a money value of more than £1000.

Silvering. After polishing, each glass tablet intended to make a looking-glass is silvered, or more correctly coated on one side with an amalgam of tin. In the preparation of this amalgam tin-foil is used, but it must be beaten from the finest tin, and possess a surface similar to that of polished silver. The art of silvering is simple, and merely requires dexterity. The glass plate having been thoroughly cleansed from all grease and dirt with putty-powder and wood-ash, the workman proceeds to lay a sheet of tinfoil smoothly upon the table, carefully pressing out with a cloth dabber all wrinkles and places likely to form air bubbles. He spreads over it a quantity of mercury, taking care that all parts are equally covered, and then the glass plate is pushed gently on to the surface, commencing at one edge. A glass plate of 30 to 40 square feet requires 150 to 200 pounds of mercury, although the amalgam is not so thick as a sheet of the finest paper. The glass is allowed to remain for twenty-four hours. It is then removed to a wooden incline similar to a reading desk, to allow of the excess of mercury draining off. As the amalgam gradually sets, the incline is increased till finally the plate reaches the perpendicular, when the process is finished, and the mirror removed to the store-room.

Silvering by Precipitation. The former method of coating the glass with tin-amalgam obtains its name of silvering by analogy only: the true process of silvering is the following, patented in 1844 by Mr. Drayton:—32 grms. of nitrate of silver are dissolved in 64 grms. of water and 16 grms. of liquid ammonia, adding to the filtered solution 108 grms. of spirits of wine of 0·842 sp. gr., and 20 to 30 drops of oil of cassia. Call this fluid No. 1. Another fluid (No. 2) is prepared by mixing 1 volume of oil of cloves with 3 volumes of spirits of wine. The workman places the glass plate upon a table, carefully levels it, and floods it to a depth of 0·5 to 1 centimetre with fluid No. 1. He then precipitates the silver by adding 6 to 12 drops at a time of fluid No. 2 until the whole of the surface is covered. For every square foot of glass 9 decigrammes of nitrate of silver are required. Liebig recommends an ammoniacal solution of fused nitrate of silver, to which 450 c.c. of soda-ley of 1·035 sp. gr. are added. The precipitate thrown down is dissolved by means of ammonia, the volume being increased to 1450 c.c., and by water to 1500 c. c. This fluid is mixed shortly before application with one-sixth to one-eighth of its volume of solution of sugar of milk, containing 10 parts by weight to 1 of sugar of milk. The glass is flooded with this fluid to about half-an-inch in depth; reduction soon sets in, and the glass becomes thickly coated. 1 square metre of glass plate requires 2·210 grms. of silver.

The plate is then dried, cleaned, and polished. Lowe employs nitrate of silver, starch-sugar, and potash; A. Martin, nitrate of silver, ammonia, and tartaric acid.

Platinising. According to the researches of Dodé, platinum may be used for coating plate-glass. In France, Creswell and Tavernier have already brought platinised mirrors before the public. Hitherto platinum has been used in ornamenting porcelain, and the glass plates are prepared in a similar manner, the metal being burnt in, as it is termed. The platinum is precipitated from its chloride by oil of lavender, the chloride being spread equally over the glass with a fine-haired paint-brush. The plate is then placed in a muffle. Cheapness is a prominent feature of this process; while all faulty glasses can be very easily repaired, those by the old methods being thrown aside as useless. In Paris the lids of boxes and fancy articles are largely manufactured from platinised glass.

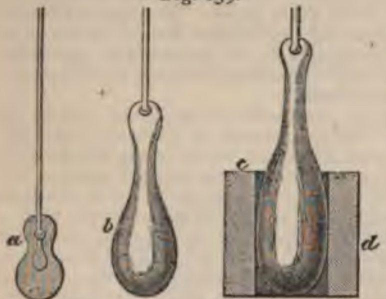
Bottle Glass. Bottle glass includes all kinds of glass made into vessels for holding fluids. It is made from common green glass, from fine white glass, and from crystal glass. Medicine bottles, &c., are made from common green glass; tumblers, or drinking glasses, from fine white glass; and crystal glass is employed for the same articles, but selling at a higher price.

The materials for ordinary bottle glass are sand, potash or soda, basalt, &c. For medicine glass the materials must be free from iron, and still purer for the articles of white glass. In the manufacture of bottle glass no considerable amount of care is required, the desiderata being strength and sufficient resistance to the action of ordinary acids. The processes of melting and annealing are conducted in the ordinary manner. The analyses of several glasses gave the following results:—

Silicic acid	74·71	74·66	75·94	74·37	74·26
Potash	—	4·32	—	12·48	—
Soda	15·74	11·01	15·15	3·42	14·06
Lime	8·77	9·13	8·01	9·02	8·60
Alumina	0·43				2·52
Oxide of iron	0·14	0·88	0·90	0·71	0·38
Oxide of manganese	0·21				0·18
	100·00	100·00	100·00	100·00	100·00
Sp. gr.	2·47	2·48	2·47	2·30	2·40

The details of the several processes of bottle glass manufacture are, after the making of the rough shape out of tough fluid glass, so various that only single examples can be given. We will select the ordinary wine-bottle. The glassblower, taking some molten glass on his pipe, turns and moulds it into the shape of *a*, Fig. 139. By continued blowing the enlarged form, *b*, is obtained; this form still more enlarged, as at *c*, is placed in the mould, *d*. The workman now blows sharply into the incipient bottle, the glass filling out the mould and producing the sharp curve of the shoulder of the wine-bottle. The rod or puntil, *e*, is now introduced, and a firm footing given by pressing in the bottom of the bottle. While the blower prepares a new bottle, the assistant places that already formed in the annealing oven. In the making of flasks and retorts the flask-tongs, Fig. 140, are employed, the neck being allowed to remain straight, as at *a*, Fig. 141, to form a flask, or bent, as at *b*, to make a retort. The manufacture of a beaker will be readily understood from Figs. 142 and 143, A, B, C, being the method of producing a globular body, and *a*, *b*, *c*, a beaker with nearly perpendicular sides. Glass-tubing is drawn out as shown at Fig. 144. Glass rods are similarly made, but without blowing.

Fig. 139.



Pressed and Cast Glass. Pressed or cast glass comprises the many cheap glass ornaments, and, indeed, ornamental glass work of all kinds, now so general. The tall, narrow-mouthed chimney ornaments are thus made by being blown into engraved brass moulds, instead of into plain moulds as in the case of the bottle. Cup-shaped articles are made with molten glass pressed between a concave and convex surface, the surplus glass escaping at some point purposely arranged. As a rule the objects taken from the moulds require but little polishing.

FIG. 140.

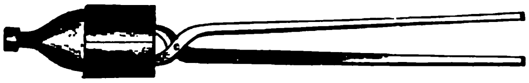
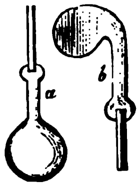


FIG. 141.



Water-Glass. By water-glass is understood a soluble alkaline silicate. Its preparation is effected by melting sand with much alkali, the result being a fluid substance, first observed by Von Helmont, in 1640.

FIG. 142.

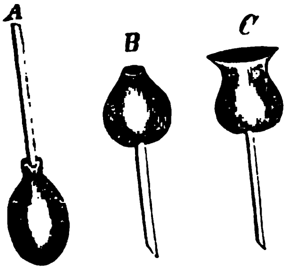


FIG. 143.

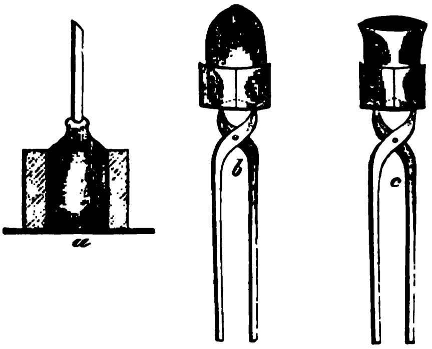
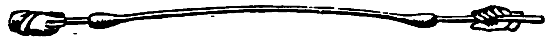


FIG. 144.



It was made by Glauber in 1648 from potash and silica, and by him termed fluid silica. Von Fuchs, in 1825, obtained what is now known as water-glass by treating silicic acid with an alkali, the result being soluble in water, but not affected by atmospheric changes.

The various kinds of water-glass are known as—

Potash water-glass.
Soda ,,
Double ,,
Fixing ,,

Potash water-glass is obtained by the melting together of pulverised quartz or purified quartz sand 45 parts, potash 30 parts, powdered wood charcoal 3 parts, the molten mass being dissolved by means of boiling in water. The solution contains much sulphuret of potassium, which is removed by boiling with oxide of copper. The addition of carbon assists in reducing part of the carbonic acid to carbonic oxide, which disappears during the melting. Soda water-glass is prepared with pulverised quartz 45 parts, calcined soda 23 parts, carbon 3 parts; or, according to Buchner, with pulverised quartz 100 parts, calcined Glauber's salt 60 parts, and carbon 15 to 20 parts. Double water-glass (potash and soda water-glass), is prepared, according to Dobereiner, by melting together quartz powder 152 parts, calcined soda 54 parts, potash 70 parts; according to Von Fuchs, from pulverised quartz 100 parts, purified potash 28 parts, calcined soda 22 parts, powdered wood charcoal 6 parts. It is further obtained by melting tartrate of potash and soda, $\left.\begin{matrix}Na\\K\end{matrix}\right\}C_4H_4O_6+4H_2O$, with quartz; from equal molecules of nitrate of potash and soda and quartz; from purified tartar and nitrate of soda and quartz. It is more fusible than the foregoing. For technical purposes a mixture of—

3 volumes of concentrated potash water-glass solution.
2 ,, ,, soda ,, ,,

is employed. By the name of fixing water-glass, Von Fuchs designates a mixture of silica well saturated with potash water-glass and a silicate of soda, obtained by melting together 3 parts of calcined soda with 2 parts of pulverised quartz. It is used to fix or render the colours permanent in stereochromy.

That known commercially as prepared water-glass is obtained by boiling the powdered water-glass with water; and the solution, as found in the market, is known as of 33° and 66°, the difference being that the first 100 parts by weight contain 33 parts by weight of solid water-glass and 67 parts by weight of water. It therefore follows that in solutions of 40° and 66°, the water is proportioned as 60 and 34 parts respectively. Acids, with the exception of carbonic acid, decompose water-glass solutions, separating the silica as a gelatinous substance; it should, therefore, be kept in vessels well set apart from volatile acids.

Water-glass is an important product in industry. It is used to render wood, linen, and paper non-inflammable. The water-glass of 33° is first mixed with double its amount by weight of rain-water, and is then treated with some fire-proof colouring matter, as clay, chalk, fluor-spar, felspar, &c. The material to be rendered uninflammable is painted with the solution, and again with another coat after the first has remained twenty-four hours to dry. Wood is thus preserved from being worm-eaten, from encrustation of fungi, &c. Another industrial application of water-glass is as a cement; in this it is equal to lime, and, indeed, is known as "mineral lime." Chalk mixed with water-glass forms a very compact mass, drying as hard as marble; no chemical change is hereby effected; there is no conversion to silicate of calcium or carbonate of potash; the hardening is entirely the result of adhesion. Phosphate of calcium treated with water-glass acts similarly. Zinc-white and magnesia lose none of their useful properties when mixed with water-glass. Another important application of water-glass is in the painting of stone and concrete walls, and in the preparation of artificial stone. The latter, first made by Ransome, is daily meeting with more extended application in England, India, and America. It is prepared by mixing sand with silicate of soda to a plastic mass, which is pressed into the required shape, and then placed in a solution of chloride of calcium. By this means siliciate of calcium is formed, and cements the grains of sand together, while the chloride of sodium is removed by repeated washings. As cement for stone, glass, and porcelain, water-glass is especially useful. It is also employed in the preparation of xyloplastic casts, made of wood rendered pulpy by treatment with hydrochloric acid, and aftewards impregnated with water-glass.

Stereochromy. An interesting and important application of water-glass is in the new art of mural and monumental painting, termed by von Fuchs *Stereochromy* (*στερεος, solid*, and *χρωμα, colour*). In this method of painting the water-glass forms the foundation or binding material of the colour. There is first to be considered the mortar or cement ground upon which the painting is to be executed. This ground has to receive an under- and an over-ground. It is essential, of course, that the fundamental groundwork should be of a stone or cement possessing every requisite for durability. The next, or under-ground, is made with lime-water, and is allowed to remain for some time to harden. When well dried the water-glass solution is applied, and allowed to soak well into the interstices of the mortar. After the under-ground has been thus prepared, the over-ground, or that to receive the painting, is laid on. This consists of similar constituents to the under-ground, with the exception that a good sharp sand is used, and the mixture treated with a thin ley of carbonate of lime. This over-ground of fine cement being nicely levelled, and having dried, it is thoroughly impregnated with water-glass. When this is dry, the painting is executed in water-colours. Nothing further is necessary than to fix these colours, which is effected by a treatment with a fixing water-glass. The colours employed are:—zinc-white, chrome-green, chrome-oxide, cobalt-green, chrome-red (basic chromate of lead), zinc yellow, oxide of iron, sulphuret of cadmium, ultramarine, ochre, &c. Vermillion is not employed, as it changes colour in fixing, turning to a brown. Cobalt-ultramarine, on the contrary, brightens on the application of the fixing solution, and is, therefore, a very effective colour. As a decorative art stereochromy will doubtless attain great importance, the paintings being unaffected by rain, smoke, or change of temperature.

Crystal Glass. Crystal glass includes all lead-containing potash glass. Crystal glass was first prepared in England. There are a few difficulties in manufacturing this glass. The smoke from an anthracite coal fire is injurious to the pure colour of the glass, so that the melting-pot is provided with a cover; but this addition has the disadvantage that the temperature necessary to melt the glass cannot easily be obtained. A larger proportion of alkali must therefore be added, which deteriorates from the quality of the glass, rendering it liable to after-change. To prevent this as much as possible oxide of lead is used to make the glass more easily fusible, and by this means a beautifully clear, transparent glass results. The following table will give some idea of the proportions of the materials:—

Sand	300
Potash	100
Broken glass	300
Minium	200
Sesquioxide of manganese	0·45
Arsenious acid	0·60

The following mixture is used in the glass houses of Edinburgh and Leith:—

Sand	300
Potash	100
Minium	150
Lead-glaze	50

And a small quantity of sesquioxide of manganese (braunite) or arsenious acid.

To render the glass fluid, saltpetre is sometimes added, but in moderate quantities. Dumas recommends sand 300, minium 200, dry potash 95 to 100. On the supposition that there is no loss during melting, the mixtures contain:—

Silica	57·4	57
Oxide of lead ..	36·3	36
Potash	6·3	7
	100·0	100

The whole melting process is included in 12 to 16 hours. The glass is treated in a manner similar to that already described, but is more easily worked. Benrath (*a*) and Faraday (*β*), found crystal glass by analysis to consist of:—

	a.	*β.*
Silicic acid	50·18	51·93
Oxide of lead	38·11	33·28
Potash	11·61	13·67
Alumina, &c.	0·04	—
	99·95	98·88

According to Benrath normal crystal glass has the formula $K_{10}Pb_7Si_{36}O_{84}$ (*i.e.*, $5K_2O,7PbO,36SiO_2$).

Polishing. Crystal glass is either cast in brass moulds or is ground. Its hardness admits of its taking a better polish than other glasses. The grinding wheel is of cast-iron; above the periphery is fixed a vessel containing water and fine washed sand, which constantly drops upon the wheel, assisting in the cutting. The polishing wheel is of wood, well served with pumice-powder and water.

Optical Glass. The preparation of good optical glass, especially in large dimensions, is a matter of much difficulty. Transparency, hardness, a high refractive power with perfect achromatism are all required, and must be obtained at the outlay of any amount of labour. The glass must also be entirely homogeneous, else the light is not refracted regularly; threads and streaks (striæ) are the results of inequality, and it naturally follows that if these appear to the unassisted eye, they will seriously affect delicate observations when high magnifying powers are used, as in telescopes and microscopes. It is an error, however, to suppose that these irregularities arise from impurities; they are rather due to interruptions in heating and cooling, or to unequally heating and cooling during manufacture. This must especially be evident in the case of waviness or an undulating structure of the glass. Crown-glass, free from lead, is not so liable to faults as flint-glass; both these are employed for optical purposes.

The Rev. Mr. Harcourt's experimental researches as to the best optical glass, communicated to the British Association at the recent meeting at Edinburgh, by Professor Stokes, show fully what has been accomplished in preparing glass of this order. Mr. Harcourt's researches were chiefly carried on with phosphates, combined in many cases with fluorides, and sometimes with tungstates, molybdates, and titanates, owing to the difficult fusibility and pasty consistency of silicate glasses. The experiments included glasses containing potassium, sodium, lithium, barium, strontium, calcium, aluminium, manganese, magnesium, zinc, cadmium, lead, tin, nickel, chromium, lead, thallium, bismuth, antimony, tungsten, molybdenum, titanium, vanadium, phosphorus, fluorine, boron, and sulphur. The molybdic glasses first prepared were of a somewhat deep colour, deteriorating with age; but at length molybdic glass was obtained free from colour and permanent. Titanic acid gave results much superior to those obtained with molybdic. Glass made with terborate of lead agreed in dispersive power with flint-glass; while a prism of this glass extends the red and blue ends of the spectrum equally with a prism of one part by volume of flint-glass with two of crown-glass. Notwithstanding the great difficulties arising from striæ, Mr. Harcourt finally succeeded in preparing discs of terborate of lead and of a titanic glass, 3 inches in diameter, almost homogeneous.

It is well known that flint- and crown-glass form an achromatic combination. Flint-glass is very easily rendered fluid, conducing to the formation of striæ. A variation of the proportions of the constituent materials, though not producing effects visible to the eye alone, will strongly striate the glass, rendering it unfit for optical purposes. The constituents must be equally distributed throughout, and this is a great difficulty. The oxide of lead being of so much greater weight sinks to the bottom, while the lighter constituents float at the upper part of the melting vessel. Usually this is so much the case that glasses of different specific gravities are obtained from the upper and lower parts of the melting-pot. Lamy has lately employed thallium flint-glass in the preparation of optical glass, thallium taking the place of potash. Cl. Winkler substitutes bismuth for the lead.

Bontemps manufactures flint glass in the following manner:—A glass mass is prepared of—

White sand	100 kilos.
Minium	106 ,,
Carbonate of potassa .	43 ,,

and placed over an anthracite or stone-coal fire in a small melting oven, shown in Fig. 145 in vertical, and in Fig. 146 in horizontal section. The oven contains only one covered melting vessel, B, standing on the bank, A. *a a* are the grate bars; *c* an iron rake, enclosed in a fire-clay cylinder, *d*, and resting upon the roller, *f*. After about fourteen hours the mass becomes equally fluid; and a red-hot rake is introduced into the vessel by which the several layers of material are intimately mixed In about five minutes the mass is sufficiently stirred; the iron rod is then removed, the clay cylinder remaining. This stirring is effected several times without removing the clay cylinder; and the glass is then ready for blowing or casting. But for optical purposes it is, after the removal of the clay cylinder, allowed to cool gradually during eight days in an annealing oven. The most perfect pieces of glass

Fig. 145.

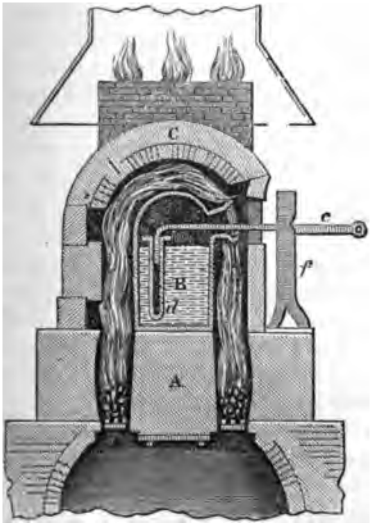
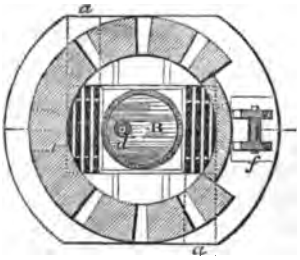


Fig. 146.



are then cut from the interior of the mass. According to Dumas's analysis of a sample obtained from Guinand, flint-glass consists of—

Silica	42·5
Oxide of lead	43·5
Lime	0·5
Potash	11·7
Alumina, oxide of iron, and protoxide of manganese	1·8
	100·0

The second kind of optical glass, crown-glass free from lead, contains, according to Bontemps :—Sand, 120; potash, 35; soda, 20; chalk, 15; and arsenious acid, 1 part.

Strass. The imitation of precious stones is an interesting feature of glass manufacture, and in Egypt and Greece it is an art that has attained to great perfection. All precious stones, with the solitary exception of the opal, can be imitated artificially. The chief constituent of these artificial gems is *strass*, or as it is termed by Fontanier, Mayence base; and in France artificial gems are mostly known as *Pierres de Strass.* This base, then, is colourless, and may be considered as a borosilicate of the alkalies containing oxide of lead, this being in larger proportion than in flint-glass.

Donault-Wieland found colourless strass by analysis to consist of:—

Silica	38·1
Alumina	1·0
Oxide of lead	53·0
Potash	7·9
Borax Arsenious acid	.. traces
	100·0

This analysis gives the formula—

$$(3K_2O,6SiO_2)+3(3PbO,6SiO_2).$$

The various gems are imitated by the addition of colouring oxides, the whole of the materials being ground to a fine powder, intimately mixed, and melted at a strong heat. The imitation of the *topaz* is obtained by taking—strass, 1000; antimony, 40; and Cassius's purple, 1 part. The topaz can also be imitated with—strass, 1000; oxide of iron, 1 part. The imitation *ruby* is obtained with 1 part of the topaz paste, and 8 parts of strass, the whole being melted together for thirty hours. A ruby of less beauty is obtained with—strass, 1000; peroxide of manganese, 5 parts. A good *emerald* can be prepared from—strass, 1000; oxide of copper, 8; oxide of chromium, 0·2 parts. The *sapphire* is obtained from strass, 1000; pure oxide of cobalt, 15 parts. The *amethyst* from—strass, 1000; peroxide of manganese, 8; oxide of cobalt, 5; Cassius's purple, 0·2. The *beryl* or *aqua marina* is imitated by—strass, 1000; glass of antimony, 7; oxide of cobalt, 0·4. The *carbuncle* by—strass, 1000; glass of antimony, 500; purple of Cassius, 4; peroxide of manganese, 4 parts. Much attention has not been paid to the mode in which the colouring is effected by the metallic oxides; nor have experiments been tried with any definite result as to the application of tungstic acid, molybdic acid, titanic acid, chromic acid, and protoxide of chromium, &c.

Coloured Glass and Glass-Staining. Coloured glass may be considered in two classes—that coloured as a whole, and that only partially coloured. The latter is prepared with such metallic oxides as will impart to the glass very intense colour; for instance, protoxide of copper, protoxide of cobalt, oxide of gold, and oxide of manganese. This kind of glass is termed superfine, and is prepared in the following manner:—Two melting vessels are placed in the oven; one contains a lead-glass, the other the coloured glass. We will take as an example glass coloured red with protoxide of copper, which if further oxidised imparts a green colour to the glass. The glass-blower dips his pipe first into the red glass, and collects a sufficient quantity to blow; then he dips this into the white glass, and proceeds to form a cylinder or roll, as in the making of table glass. Superfine glass is known as "outside" and "double," or "double layer." In the first case the workman takes a lump of white glass upon his pipe and covers it with the coloured glass; or, in the second case, he takes up only a small quantity of white glass, then sufficient of the coloured glass, and again more white glass. Red glass may be obtained with either Cassius's purple, protoxide of copper, or oxide of iron as the colouring ingredient. Cassius's purple is used chiefly for ruby-red glass. It was long thought that ruby-coloured glass could not be obtained with any other preparation than Cassius's purple, but twenty-five years ago Fuss showed that chloride of gold was effectual. If glass containing salts of gold or protoxide of copper is cooled suddenly, the colour disappears; then if again gently warmed, not quite to softness, the colour suddenly reappears in full splendour. This phenomenon occurs equally in atmospheres of oxygen, hydrogen, and carbonic acid. In the preparation of protoxide of copper glass, lead-glass is taken as a basis, to which 3 per cent. of the protoxide is proportioned. The drawback to the employment of the protoxide is the readiness with which it becomes oxide, this imparting a green colour to the glass. To prevent this change iron filings, rust, or tartar is added, or the glass is stirred with green wood. Copper-glass, as has just been said, is colourless on cooling, regaining its colour during the process of annealing. Oxide of iron, known commercially as blood-stone, ochre, or red chalk, is also used to impart a red colour. Yellow and topaz-yellow are obtained by means of antimoniate of potash or glass of antimony, chloride of silver, borate of oxide of silver, and by sulphuret of silver. Oxide of uranium imparts a green-yellow. Blue is obtained from oxide of cobalt, more seldom by means of oxide of copper. Green results from the addition of chrome-oxide, oxide of copper, and protoxide of iron. Violet is obtained from oxide of manganese (braunite) and saltpetre; black, from a mixture of protoxide of iron, oxide of copper, braunite, and protoxide of cobalt. A beautiful black results from sesquioxide of iridium.

Glass Painting. The delineation of figures and scriptural events in coloured glass dates from a very remote period. At first the work was merely mosaic, pieces of coloured glass being inserted in leaden framework. Glass painting was known in Germany in the middle ages, and soon extended throughout Europe. In the 13th century, when Gothic architecture became prevalent, glass painting also became more general, as until then the heavy, round-arched windows were too small to admit of ornament. But it was not until the 15th century that the heavy outlined figures were discarded for the more mingled colours of heraldic device, as seen in the churches of Sebaldus and Lorenz, of Nuremburg, in the productions of the celebrated Hirschvogel family. This style lasted till the 16th century, when the glass-maker tried the effect of pigments upon glass. Since that time the art has gradually improved, the improvement at first being most manifest in France and the Netherlands.

The nature of glass-painting or staining is in principle the following:—When coloured glass, rendered easily fusible by the metallic oxide it contains, is finely pulverised, and laid upon a plain glass surface and heated, it forms a skin, or "flash," as it is termed, this skin or layer of glass being said to be "flashed on." It is evident that very brilliant effects may thus be attained. The near surface of the glass receives the strong shades and colours, the other or distant surface the lighter tints. White was not employed in the older glass paintings, but is now used in the flesh-tints, pure white effects, &c. Oxide of tin and antimoniate of potash yield a good white. For yellow, Naples-yellow, or antimony-yellow, or a mixture of the oxides of iron, tin, and antimony, or of antimonic acid and oxide of iron, of sulphuret of silver and sulphuret of antimony, or chloride of silver is used; for red, oxide of iron, purple of Cassius, and a mixture of oxide of gold, oxide of tin, and chloride of silver; for brown, oxide of manganese, yellow ochre, umber, and chromate of iron; for black, oxide of iridium, oxide of platinum, oxide of cobalt, and oxide of manganese; for blue, oxide of cobalt, or potassium-cobalt nitrate; for green, the oxides of chromium and copper. Two kinds of colours are distinguished, the hard and the soft. The soft are called varnish colours, are not very easily fluid, forming a kind of glaze upon the glass. These colours are placed upon the outer surface. The hard or decided tints are semi-opaque, and are placed upon the inner surface of the glass. The binding fluid or vehicle is a mixture of silica, minium, and borax, with which the colour, being previously ground to a fine powder, is intimately mixed. This mixture is painted on the glass with a pencil, and the glass plate is afterwards fired in a muffle. Recently volatile oils have been employed as a vehicle, viz., oil of turpentine, lavender, bergamot, and cloves. The burning-in, or firing, the colours was formerly effected by placing the glass tablet with dried and pulverised lime in an iron pan raised to a red heat. But recently the muffle oven has been employed. The bottom of the muffle is covered to a depth of one inch with dry powdered lime, upon which the plate of glass is laid, and again a layer of lime. The oven is then raised equally to a dark red heat. After six to seven hours the fire is gradually withdrawn, and the oven allowed to cool. The glass is taken out, cleansed with warm water, and dried.

Enamel. Bone Glass. Alabaster Glass. By enamel is understood in glass manufacture a coloured or colourless glass mass rendered opaque by the addition of oxide of tin. It formerly was prepared in the following manner:—An alloy of 15 to 18 parts tin and 100 parts lead was oxidised by heat in a stream of air, the oxide pulverised and washed. The mixture of the oxides was then fritted with the glass. An enamel-like appearance is imparted to glass by arsenious acid, chloride of silver, phosphate of calcium, cryolite, fluor-spar, aluminate of soda, and precipitated sulphate of barium. Bone glass, so-called, is a milk-white, semi-opaque glass, containing phosphate of calcium in the shape of white bone-ash, sombrerite, or phosphorite. It is employed for lamp-globes and shades, thermometer scales, &c. It is made by adding to white glass about 10 to 20 per cent. of white bone-ash, or a corresponding quantity of mineral phosphate. After melting the glass is generally clear and transparent, becoming milk-white and opaque during the process of blowing. The colour is finally developed during annealing. A similar glass to the preceding is alabaster glass, but the latter is more opaque. It is also termed opal glass, rice glass, or rice-stone glass, and Réaumur's porcelain. The materials are the same as in the preparation of crystal glass, of which it may be considered the scum or underlayer of impurities, though it is really imperfectly prepared crystal glass.

Cryolite Glass. Cryolite glass, or hot-cast porcelain, has recently been manufactured in Pittsburg. It is a milk-white glass, obtained by melting together

Silica..	67·19	per cent.
Cryolite	23·84	,,
Oxide of zinc	8·97	,,

Fluor-spar or aluminate of sodium may be substituted for cryolite. Benrath found (1869) in such a milk glass—

Silica	70·01	per cent.
Alumina..	10·78	,,
Soda	19·21	,,
	100·00	

Ice Glass. Ice glass is made by plunging the mass of glass attached to the end of the blower's pipe, still at a glowing red-heat, into hot water, in which the glass is opened and blown out. It then resembles a mass of thawed ice, with a beautifully pellucid appearance. It is also known as crackle-glass; in France, as *verre craquette.* Agate glass is obtained by melting together the waste pieces of coloured glass.

Hæmatinon. Astralite. This is a glass resembling that found in the Pompeiian excavations, and mentioned by Pliny. It possesses a beautiful red colour, between that of vermillion and of minium, is opaque, harder than ordinary glass, bears a high polish, and has a sp. gr. = 3·5. The colour is lost by melting, and by no addition can be recovered. The glass contains no tin or protoxide of copper as a colouring matter. Von Pettenkofer assimilated to this glass by melting together silica, lime, burnt magnesia, litharge, soda, copper hammerings, and smithy scales. A part of the silica in the mixture is decomposed by means of boracic acid, and a mass is obtained which, when ground and polished, exhibits a dark red colour of great beauty. Pettenkofer gave to this glass the term astralite, from the beautiful shotte-colour of blue or dichromatic tint shimmering throughout the mass.

Aventurin Glass. Aventurin or avanturin glass was formerly made only in the Island of Murano, near Venice, but is now prepared throughout Germany, Italy, Austria, and France. It is a brown glass mass in which crystalline spangles of metallic copper according to Wöhler (of protoxide of copper according to von Pettenkofer) appear dispersed. Fremy and Clemandot have produced a glass similar to aventurin glass, and which consisted of 300 parts glass, 40 parts protoxide of copper, and 80 parts copper-scale. The Bavarian and Bohemian glass-houses produce an aventurin glass rivalling the original. Von Pettenkofer has prepared aventurin glass direct from hæmatinon by mixing sufficient iron-filings with the molten mass to reduce about half the copper contained. Pettenkofer surmises, and with good reason, that aventurin glass is a mixture of green protoxide of copper glass with red crystals of silicate of protoxide of copper, these complementary colours giving the brown tint. This glass is also well imitated by melting a mixture of equal parts of the protoxides of iron and copper with a glass mass. The protoxide of copper appears after a long annealing as a separate, crystalline, red combination, while the protoxide of iron is lost in the green colour it imparts to the glass. Pelouze found that by freely adding chromate of potash to the glass materials spangles of oxide of chromium were separated. He termed this glass chrome-aventurin; it has been employed by A. Wächter in the glazing of porcelain.

Glass Relief. Glass relief is obtained by enclosing a body of well-burnt unglazed white clay, moulded to the required form between layers of lead-glass, the result being similar in appearance to an article in matted silver. Gold matte is imitated by employing a yellow glass. This branch of their art has been known to the Bohemian glass manufacturers for upwards of eighty years.

Filigree, or Reticulated Glass. By fibre or filagree glass is understood that kind of glass work formed of variously coloured or white opaque glass threads, these threads being sometimes as fine as a single hair. They are generally drawn out from tubes or sticks of glass of various colours, heated to redness, and formed into sticks, tubes, or spirals. Two of these tubes are taken, placed together, and blown out into a vessel of the required form, which is characterised by the conformation of the glass threads in the stick. From the spiral network thus formed this kind of glass is sometimes termed reticulated.

Millifiore Work. Millifiore work is a peculiar form of mosaic glass work, in preparation similar to that of Petinet glass. Small filagree canes of different coloured glass are placed side by side to form a thick cord or column, the cross section of which appears of a parti-coloured grain. These cords or columns can be twisted to almost any required form, or when heated and drawn out the glass threads of various colours of which it is composed form a single thread of very varied hue and great beauty. These threads again can be worked into ornaments, or formed into lumps or balls. The best kind of millifiore work are the paper-weights, often sold at fancy bazaars as Bohemian glass weights—these are merely lumps or rolls of the many-coloured glass thread placed together, heated, and finally coated with a film of clear white glass by being for a few moments held in the white glass melting-pot.

Glass Pearls. There are two kinds of artificial or glass pearls, namely, solid or massive pearls and blown pearls. The first are known as Venetian pearls, and those made in Venice are preferred, the export from this city in 1868 representing a money value of 7,755,000 francs. The manufacture is chiefly carried on in the Island of Murano. The pearls are made from small glass tubes, either white or coloured. Oxide of tin is employed in the preparation as well as the various metallic oxides for imparting the desired colours.

Solid Pearls. The glass tubes are cut into small pieces or cylinders. The sharp edges of these cylinders are removed by placing them in an iron vessel brought to a red heat, the beads being constantly stirred with an iron spoon. Previous to this operation the interior or hollows of the beads are filled with powdered charcoal. They are then well washed, dried, and packed. By another mode of preparation the pieces of glass tubing are placed in a revolving vessel similar to a coffee-roaster. The finished pearls are generally strung, the charcoal being placed in the interior or tube of the bead to prevent its closing.

Blown Pearls. The preparation of blown pearls is quite a distinct manufacture. They resemble the real pearl in form, colour, and surface. Jaquin, a French paternoster or rosary maker, in the year 1656, remarked that when whitings (*Cyprinus alburnus, ablettes*) were washed with water, a residue remained consisting of a beautiful pearly substance. This was the foundation of the manufacture of the artificial pearl. Jaquin scaled the fish, mixed the scales with water, and obtained the celebrated "*Oriental pearl-essence*," or "*Essence d'Orient*," a substance identical with *Guanin*. A small bead of gypsum or other hardening paste is coated with this mixture, dried, and dipped into molten glass, a thin film of which adheres.

The pearl is sometimes round, sometimes pear-shaped, or flat. Another method of preparing the pearls is by means of beads blown from glass tubes of various thicknesses. These beads or small bulbs are then filled with pearl-essence. To prepare this essence, say a quantity of 120 grms., 4000 fish are necessary; thus a pound of pearl-essence requires 18,000 to 20,000 fish for its preparation. The scales are allowed to stand about an hour in water to permit the slimy matter adhering to them to settle; they are rubbed down in a mortar with fresh water, and strained through a linen cloth. Thus prepared the paste is ready for insertion in the glass beads, a little ammonia being added to prevent decay.

Hyalography. Hyalography, or the art of etching on glass, is due to one Heinrich Schwankhardt or Schwandard, an artist living at Nuremburg in 1670. It consists of the following operations:—Powdered fluor-spar is treated with concentrated sulphuric acid in a leaden vessel; gentle heat is applied, the vessel being covered with the glass plate to be etched coated with wax, through which the design is traced with a steel etching-needle. Vapours of hydrofluoric acid (FlH) are evolved, which combine with the silica of the glass, forming fluoride of silicon, $SiFl_2$, and volatilising. The plate is afterwards washed with warm oil of turpentine. The first practical application is due to Hann, of Warsaw, in 1829. More recently, Böttger and Brömeis, with Auer, of Vienna, have improved the processes. The etching-ground used for engraving on metallic surfaces would not in this case give favourable results. Pül recommends a molten mixture of 1 part asphalt and [illegible] part colophonium, with so much oil of turpentine as will bring the mass to the consistency of a syrup. Etched glass plates have been used by Böttger and Brömeis to print from instead of steel and copper. In the press the glass plate is backed by a cast-iron plate. The process, however, has not been practically successful; it is better suited to the production of bank notes, &c., than engravings, the resulting etchings being hard in tone. But for purposes of decoration, etched glass is largely used. By the method of Tessié du Motay and Maréchal of Metz, a bath is made of 250 grms. of hydrofluoride or fluoride of potassium, 1 litre of water, and 250 grms. of ordinary hydrochloric acid. Kessler employs a solution of fluoride of ammonium.

CERAMIC OR EARTHENWARE MANUFACTURE.

Clays and their Application. Felspar.

To the most important alumina combinations found native belongs felspar. This mineral is one of the chief members of the class containing gneiss, granite, and porpyhry. Potash-felspar, $\left.\begin{matrix}3\text{Si}\\ \text{AlK}\end{matrix}\right\}O_8$, with 6·54 parts of silica, 18 alumina, and 16·6 potash, is also known as *orthoclase* or *adularia;* when sodium takes the place of potassium, the felspar *albite* is formed. According to Mitscherlich some felspars contain 0·4 to 2·25 per cent. of barium. When felspar is under the influence of water and carbonic acid with changes of temperature, it loses its silicate of potash, which being washed out, the potash is taken up by plants, and will perhaps account for some portion of the potash always present in their ash; some of the silicate is acted upon by carbonic acid, by which the silicic acid is separated and soluble carbonate of potash formed. In following this decomposition to a conclusion, we may surmise that the silicic acid thus set free becomes a constituent of the opal and chalcedony spar. All clays are essentially silicate of alumina; and in many instances, as in Devonshire and Cornwall, the change from felspar of the fine white granite to clay by disintegration is very perceptible. By washing this clay to free it from quartz and mica a fine white clay is obtained, known as kaolin or porcelain clay. Again, by washing with potash ley, whereby the free silica is taken up, there is obtained, in most cases, a fine plastic mass, consisting of 1 molecule of alumina, 1 molecule of silica, and 2 molecules of water. The quantity of free silicic acid varies between 1 to 14 per cent.

Kaolin, or Porcelain Clay.

The weathering of the felspar may be formulated thus—

1 mol. felspar, Si_3O_8KAl, or $\left.\begin{matrix}3\text{Si}\\ \text{AlK}\end{matrix}\right\}O_8$

gives, under the influence of water,

1 mol. porcelain clay, ${}_2SiO_4HAl$, and
1 „ acid silicate of potash,

the latter forming a soluble combination similar to water-glass. Porclain clay occurs in the following localities:—1. Bavaria: Aschaffenburg, Stollberg, Diendorf, Oberedsdorf. 2. Prussia: Morl and Trotha, near Halle (material for Berlin porcelain manufacture—decomposed or disintegrated porphyry). 3. Saxony: near Schneeberg and Mionia. The first is a weathered granite; the latter, porphyry. 4. Eastern Hungary: Brenditz in Moravia; near Carlsbad, Bohemia; Prinzdorf in Hungary. 5. France: St. Yrieux, near Limoges. 6. England: St. Austell, in Cornwall. Weathered granite; a mixture of orthoclase and quartz. It is found chiefly on Tregoning Hill, near Helstone. 7. China. It naturally follows that the clay should contain foreign substances; and it is from the quality and quantity of these substances that the several varieties of clay are obtained, of course with due reference to the chief constituents—silicic acid and alumina. The purer clays contain generally the following foreign substances:—Sand, partly as quartz sand, as silicate of potash, and partly as particles or fragments of undecomposed minerals; baryta combinations; carbonate of magnesium; carbonate of calcium; oxide of iron; sulphur pyrites; and organic matter.

The Technically Important Qualities of the Clays.

For the technical application of the clays the important qualities are colour, plasticity, and well hardening under heat.

Colour. Naturally clays are white, yellow, blue, or green. Pure clay is white; coloured clays are the result of several admixtures. White clay contains but a small quantity of protoxide of iron, and becomes after burning yellow or red; these colours originating from the organic substances disappear on their being volatilised after many firings. The coloured clays change their colour during firing, becoming red or red-yellow. Fine clays are prepared only from those becoming white by continued burning.

Plasticity. The clay should absorb water readily, forming a tenacious mass, capable of taking sharp and clear impressions. It is clear that the plasticity of the clays depends in a great measure on their composition. Sand is the constituent most prejudicial to plasticity, lime less so, and oxide of iron least of all. Clay possessing a high degree of plasticity is said to be *fat* or *long*, and when in the opposite condition *lean*, *thin*, or *short*. All *shrunk* clays, that is, all clays decreased in volume by burning, are said to be either *drawn* or *burst*. The amount of shrinkage depends of course upon the quantity of water the clay contains; the same kind of clay does not always exhibit the same shrinkage. Fat clays shrink more than short clays. The diminution in surface by shrinkage varies between 14 and 31 per cent., the capacity or solid contents between 20 and 43 per cent. Clay may be burnt so hard as to give sparks when struck with steel; but its property to form a plastic mass with water is then wholly lost. Pure clay (silicate of alumina) is by itself infusible, but by mixture with lime, oxide of iron, and other bases becomes more or less easily fusible. According to the experiments of E. Richters (1868) the refractory qualities of clay are least influenced by magnesia, more so by lime, still more by oxide of iron, and most by potash. Fusible clay obviously is not adapted to the manufacture of porcelain or such ware as is likely to be exposed to a high temperature. A fusible and a refractory clay, when heated together, enter into a mass that does not cleave to the tongue. By the manufacture of clay ware, then is understood the binding of certain clays together by means of a suitable flux.

Kinds of Clay. The clays employed in ceramic manufacture are—

1. Refractory clays: as porcelain and plastic clays.
2. Fusible clays; as potter's clay.
3. Limey clays; as marl, loam.
4. Ochre clays; as ruddle, ochre.

Of these porcelain clay is the most important; it is of various colours, very tenacious, plastic to a high degree, burns white, and is not fusible in a porcelain-oven fire. It is ordinarily found in the tertiary formation, almost always accompanied by other kinds of clay, by quartz-sand, and by brown coal. For practical purposes it is important to know that clays of the same strata and of the same pit often differ largely in their refractory property. This is not only the result of experience, but of a lengthy series of experiments made by C. Bischof, Otto, and Th. Richters. The strata near Klingenberg-on-the-Maine, at Coblenz, Cologne, Lautersheim, and Vallendar-on-the-Rhine, Weisboch in Baden, Bunzlau in Silesia, Schwarzenfeld near Schwandorf, and Kemnath in Bavaria, in the province of Hessen, in Saxony, in Belgium, near Dreux in France, and Devonshire and Stourbridge in this country, are all celebrated for this clay. The following analyses give the composition of various refractory clays:—

	1.	2.	3.	4.	5.
Silica	47·50	45·79	53·00	63·30	55·50
Alumina ..	34·37	28·10	27·00	23·30	27·75
Lime	0·50	2·00	1·25	0·73	0·67
Magnesia ..	1·00	—	—	—	0·75
Oxide of iron	1·24	6·55	1·75	1·80	2·01
Water	1·00	16·50	—	10·30	10·53

1. Almerode in Kurhessen (crucible). 2. Schildorf near Passau (graphite crucible). 3. Einberg near Coburg (porcelain capsule). 4. Stourbridge. 5. Newcastle (fire-brick).

The composition of the Stourbridge fire-clay will be seen from the following analyses by Professor F. A. Abel, F.R.S., Chemist to the War Department:—

Sample.	Silica.	Alumina.	Peroxide of Iron.	Alkalies, Waste, &c.
1	66·47	26·26	6·63	0·64
2	65·65	26·59	5·71	2·05
3	65·50	27·35	5·40	1·75
4	67·00	25·80	4·90	2·30
5	63·42	31·20	4·70	0·68
6	65·08	27·39	3·98	3·55
7	65·21	27·82	3·41	3·56
8	58·48	35·78	3·02	2·72
9	63·40	31·70	3·00	1·90

The sample No. 9, containing only such a small quantity of iron, is much superior to No. 1, whose refractory properties may be doubted. The clay is dug from pits varying from 120 to 570 feet in depth. It is generally found below three workable coal measures, between marl or rock and an inferior clay. The seam averages 3 feet in thickness, never exceeding 5 feet, and the middle of the seam contains the clay selected for crucibles, &c. Pot-clay or crucible-clay only occurs in small quantities, and costs at the pit-mouth 55s. a ton, ordinary fire-clay only realising 10s. a ton,

Potter's Clay. Ordinary potter's clay also possesses most of the properties of plastic clay; many varieties form with water a similarly tenacious mass. But potter's clay is highly coloured, retaining the colour after burning. It effervesces on the application of hydrochloric acid, and changes to marl. It follows from its containing large proportions of lime and oxide of iron that it is fusible, and melts according to the quantity of these constituents at a higher or lower temperature into a dark coloured, slag-like mass. It is found in the last formation, or entirely on the surface of the earth, and sometimes in the tertiary formation. It contains among other foreign substances organic matter, iron and other pyrites, gypsum, &c.

Walkerite. Walkerite, or Walker's clay, is a soft, friable mass, occurring from the weathering of Diorite and Diorite slate. In water it separates to a powder, not forming a plastic pulp. In its powdered condition it is of use as an absorbent of fat, &c., whence its application to the removal of grease spots in books, &c. It is found at Reigate in Surrey, Maidstone in Kent, further at Aix-la-Chapelle, in Saxony, Bohemia, Silesia, and Moravia. It is employed in paper-making, and as an addition to ultramarine.

Marl. Marl is a mechanical mixture of clay and carbonate of calcium, containing sand (sand-marl), and other constituents; that containing lime is called lime-marl;

that clay, clay-marl. In water it falls to powder, and forms a non-adhesive, pasty mass. With acids it effervesces, whereby more than half the weight is lost. It melts easily. It is found in the lias and chalk formation. Its chief application is to the improvement of land.

Loam. Loam may be considered as the result of the mixture of clay with sand. It is a clay more or less mixed with quartz-sand and iron-ochre, also with lime, when it assumes a yellow or brown colour, changing on burning to a red. It forms with water a slightly plastic mass, and is not very refractory. It is found always on the surface of the earth, and known as common clay, employed in the manufacture of bricks, coarse pottery, &c.

There is sometimes, but very seldom, used in earthenware manufacture, a mixture of clay and iron-ochre or hydrated oxide of iron ($2Fe_2O_3,3HO$).

Composition of Kaolin. Kaolin in pure condition, and only by means of washing, freed from coarse substances, quartz, sand, &c., is a mixture of porcelain clay with rocky residue. Porcelain clay, *i.e.* the plastic part of kaolin, is always of equal composition. The composition of kaolin is given in the following analyses:—

From.	Rocky residue.	Silica.		Alumina.	Water.
		Free.	Combined with Alumina.		
St. Yrieux	9·7	10·9	31·0	34·6	12·2
Cornwall . ..	19·6	1·2	45·3	24·0	8·7
Devonshire	4·3	10·1	34·0	36·8	12·7
Passau	4·5	9·7	36·7	37·0	12·8
Aue	18·0	1·7	34·2	34·1	11·0
Morl, near Halle .	43·8	4·4	21·6	22·5	7·5

Kinds of Clay Ware. Clay ware is generally separated into *dense* and *porous* ware. The dense ware is so strongly heated that half its mass is lost; its fracture is glazed and conchoidal; it is translucent and compact, being impenetrable to water; and it gives a spark when struck with steel. Porous clay ware is, in the mass, not glazed, its fracture open and earthy; and, when not superficially glazed, water freely percolates through it. It also clings to the tongue. The burnt mass, whether dense or porous ware, either remains rough or is glazed.

The following are the essential varieties of clay ware:—

I. *Dense Clay Ware.* A. Hard porcelain. The mass equal throughout; not indented with a knife; fine-grained, translucent, sonorous, and white. Fracture, fine-grained, and conchoidal. Sp. gr. = 2·07 to 2·49. It may be considered as composed of two substances—namely, as a natural clay or true kaolin, infusible, and preserving its whiteness under a strong heat; and as a flux consisting of silica and lime, or felspar, with or without gypsum, chalk, and quartz. The glazing is essentially due to this flux, and not to oxide of lead or tin. It is characteristic of the manufacture of hard porcelain that the burnings are included in *one* operation.

B. Soft or tender porcelain. The mass more easily fluid than hard porcelain. Two kinds are known:—

a. French porcelain, a glass-like mass, essentially a potash-alumina silicate, prepared with the addition of clay, therefore erroneously termed a clay ware, and containing lead similarly to crystal glass.

β. English soft porcelain. The mass similar to kaolin, plastic, remaining white when burnt (pipe-clay). It is made with a vitreous grit, consisting of gypsum, Cornish stone (weathered pegmatite), bone-ash (essentially phosphate of calcium), in very varied proportions. The glaze is obtained by pulverised Cornish stone, chalk, powdered fire-clay, and borax, mostly with, seldom without, the addition of oxide of lead. The glazing is a second process.

C. Statue porcelain, or biscuit ware:—

α. Genuine and unglazed porcelain.

β. Parisian porcelain, or parian. Unglazed statue porcelain is similar to English porcelain.

γ. Carrard, less translucent than parian, and sometimes of a whiter colour.

D. Stoneware. Dense, sonorous, fine-grained, homogeneous, only in the least, if at all, translucent, white or coloured.

α. Glazed porcelain stoneware. Plastic, remaining white after burning, slightly refractory with the addition of kaolin and fire-clay; a felspar as flux; the glaze contains borax and oxide of lead.

β. White or coloured unglazed stoneware. Wedgwood ware.

γ. Common stone-ware (salt-glazed). No fluxing material is employed, but the firing is increased. Glazed with siliceous soda-alum.

II. *Porous Clay Ware.* A. Fine Fayence with transparent glaze. The body earthy, clinging to the tongue, non-transparent, sometimes sonorous; the glaze containing lead, borax, felspar, &c.

B. Fayence, with non-transparent glaze. The body of a yellow burnt potter's clay or clay-marl, with non-transparent white or coloured glaze or enamel, containing tin. To this class belongs majolica, delf ware, &c.

C. Ordinary potter's ware. The body of ordinary potter's clay or clay-marl, red-coloured, soft, and porous. Mostly glazed with lead, the glaze being always non-transparent. According to the colour of the glaze, the ware is distinguished as white and brown.

D. Plate, terra-cotta, fire-clay ware, tubes, ornaments, vases, &c. The body earthy; mostly more or less unequal; always coloured, porous, easily fluid, and slightly sonorous. Is not usually glazed.

I. Hard Porcelain.

Grinding and Mixing the Material. Hard porcelain is composed of a mixture of colourless porcelain clays with felspars as a flux, which sometimes is composed of quartz, chalk, or gypsum. The porcelain clay, in itself infusible, and becoming in the fire only an earthy, opaque mass, when intimately mixed with the flux material, melts easily at a higher temperature than that of the glass oven. The materials of porcelain manufacture are not found native in such a condition that they may at once be employed; they must be ground to a fine powder, and this washed to separate the foreign substances. Pure kaolin, however, is not utilisable in porcelain manufacture, as it becomes much decreased in volume on the application of heat. It is therefore mixed with fine washed quartz sand, although this addition somewhat impairs the plasticity. This mass on treatment with fire would be porous, and it is for the closing of the pores and to form a binding glass that felspar is added. The proportions in Berlin porcelain, according to G. Kolbe (1863), are 66·6 parts silica, 28·0 parts clay, 0·70 part protoxide of iron, 0·6 part magnesia, and 0·3 part lime.

Proportions of the materials as employed at—α. Nymphenburg; β. Vienna; γ. Meissen:—

α.	Kaolin from Passau	65
	Sand therewith	4
	Quartz	21
	Gypsum	5
	Broken biscuit ware	5
β.	Kaolin from Zedlitz	34
	Kaolin from Passau	25
	Kaolin from Unghvar	6
	Quartz	14
	Felspar	6
	Broken ware	3
γ.	Kaolin from Aue	18
	Kaolin from Sosa	18
	Kaolin from Seilitz	36
	Felspar	26
	Broken ware	2

The mixture of the materials in the required proportion takes place in large vats, whence the thin pulp is pumped and forced through sieves into another vessel.

Drying the Mass. After the water is removed from the sediment at the bottom of the vat or tank, the clay appears as a slime, which has to be dried to the required consistency. The drying or evaporation of the water is effected in wide wooden tanks exposed to a strong current of air. This is a very general method of drying the mass, but can only be employed during the summer months on account of the dampness of our climate. It is not, therefore, sufficiently extensive for large manufacturers, and consequently other means of drying are resorted to—usually by means of absorption, the mass being laid on a porous layer of burnt lime, gypsum, &c. Drying by means of gypsum is expensive, as it soon becomes hardened, and has to be removed. The mass can also be dried by means of air-pressure, being in this case placed in flat porous boxes, under which a vacuum chamber is situated. Talbot's apparatus is formed on this principle. In Grouvelle and Honoré's system of drying, the water is first partially removed, by means of draining over gypsum, and the mass is then put into firm hempen sacks, which are subjected to pressure in a screw or lever press. Pressed clay has greater plasticity than that dried by artificial heat; but the method is expensive, as the sacks soon require replenishing, being speedily worn out by the constant pressure. **Kneading the Dried Mass.** When the mass is dried by pressure or by absorption, the water in all cases is not equally expelled, and there are also air-bubles, which must be removed. This is done by kneading and treading the mass with the feet and hands, and by this means also the plasticity of the mass is improved. Another method of improving the plasticity is by allowing the moist clay to stand till it becomes putrid. Stagnant water is often employed. Brongniart explained the action of this rotting, as it is termed, to be that gases were formed in the body of the clay, and that by the continuous movement caused in their endeavour to escape, the finest particles of the material were intimately mixed. Salvêtat gives the following hypothesis:—By the rotting there is formed in the mass a large quantity of sulphuretted hydrogen gas. This gas effects the reduction of the alkaline sulphurets to sulphuret of calcium under the influence of the organic substances, the sulphuret of calcium being set free, a similar action taking place with the carbonic acid in contact with the air. The bleaching of the mass on exposure to the air is due to the oxidation of the black sulphuret of iron to sulphate of iron, which is removed by washing. The decomposition of the felspar constituents may also ensue from the long-continued action of the water. According to E. von Sommaruga, of Vienna, the existing sulphates are decomposed by the air into sulphuretted hydrogen and carbonated salts, and these being removed with the water, the refractory nature of the clay is improved.

The Moulding. The kneading and rotting accomplished, the porcelain mass is taken to another room to be moulded. This is effected either on a potter's wheel or in a mould.

The Potter's Wheel. The potter's wheel consists of a vertical iron axis, on which a horizontal solid wheel is fixed, and caused to revolve by the feet or by steam-power, the motion in the latter case being regulated by the feet. A lump of clay is placed upon the wheel, the thumb being placed in the centre of the lump and pressed downwards; a hollow is thus formed, which is widened, or the walls continued vertically according to the shape of the vessel to be made. The constant revolution of the wheel easily allows of the moulder obtaining a perfectly cylindrical form. By thus humouring the clay, elongating the vessel, again depressing it, widening it, and by continued manipulation in this manner, the most exquisite shapes are produced. To form the ridges or sharp edges of the vessel a small piece of iron, a strip of horn or wood, termed a bridge, is used. The perfectly formed vessel is cut away from the wheel by a piece of brass wire.

Moulding in Plaster of Paris Forms. A mould is first taken from the pattern or original object, which may be of clay, wax, gypsum, or metal. The moulding is performed with dry material, with clay of the consistency of dough, or with fluid clay. The moulds must possess a certain amount of elasticity, and be porous in order to absorb the moisture expressed. For these reasons plaster-of-Paris is generally used. The mould is taken from the original article in parts, which are trimmed to fit together accurately; into each part is then pressed sufficient clay to fill the indentations of the pattern, more clay being added till a proper thickness is obtained. The parts are then fitted together, and the moulds left for some time. This method of moulding is sometimes called presswork, and is adapted to all kinds of pottery not of circular form. Plates, cups, and dishes are also made in a similar manner. A leaf of clay is rolled out and pressed between flat moulds. Sometimes, instead of rolling, the clay is beaten out with a wooden hammer covered with leather.

Casting. Moulding porcelain articles out of thin pulpy clay is one of the most ingenious arts of the potter. The fluid clay is poured into porous moulds, which absorb a portion of the water, thereby reducing the pulp to a certain consistency. The interior pulp remaining fluid is now poured out, and the cast or coating of clay adhering to the mould allowed to harden. When sufficiently hard the vessel is taken to the lathe to be finished, or if not of circular form, to the finishing room, where with sharp tools any required pattern is cut, or handles, spouts, &c., which have been made in separate moulds, attached.

Preparation of Porcelain Articles without Moulds. The finest porcelain is finished by hand, as machinery or moulds could not give sufficient sharpness to the beautiful flowers and figures sculptured on vases, &c. The flowers, &c., are first prepared in moulds, are then attached to the body of the article, and finally are finished off with edged tools. The stalks of the flowers are sometimes formed on wire; and the leaf is first roughly constructed in the palm of the hand, the furrowing and veining being done afterwards. The texture of drapery is imitated by means of a piece of tulle, which is laid on the clay, and allowed to dry. During the burning the tulle is consumed, leaving the pattern on the porcelain.

Drying the Porcelain. After the porcelain ware is formed, it is dried for some time at the ordinary temperature. This is continued till the clay contains no moisture, that is, until its weight is tolerably constant. During this drying the clay is said to be in the green state, and possesses a greater tenacity than it has in any of the former processes.

Glazing. Only very few articles of porcelain ware, generally statues or figures, remain unglazed; these are termed *biscuit ware*. All other articles are glazed. The glazings employed are of four kinds:—1. Earth or clay glazings are transparent, and formed by melted silica, alumina, and alkalies; they easily become fluid, and melt about the temperature at which the vessels are baked. This kind of glazing is used for hard porcelain. 2. Lead glazes are transparent glazes containing lead; most of these melt at the temperature at which the articles are burnt. 3. Enamel glazes are partly white, partly coloured opaque glasses containing oxide of tin besides oxide of lead. This kind of glaze is easily melted, and serves to cover the unequal colour of the under mass. 4. Lustres are mostly earth and alkali glazes. This class includes the ordinary salt-glazed ware, as well as glazes containing metallic oxides used to imitate gold and silver surfaces for ornament merely.

Porcelain Glaze. We will here, however, concern ourselves only with porcelain glaze. It is necessary that this glaze should melt readily at the temperature at which the article is fired; that it should be colourless and opaque; that it should fire sufficiently hard to withstand pressure, grinding, and ordinary cutting. The glaze is added to the porcelain mass with a flux, so that the melting may be readily effected. At Meissen the glaze used contains:—

Quartz	37·0
Kaolin from Seilitz	37·0
Lime from Pirna	17·5
Broken porcelain	8·5
	100·0

In the Berlin porcelain manufacture the following glaze is employed:—

Kaolin, from Morle, near Halle	31
Quartz-sand	43
Gypsum	14
Broken porcelain	12
	100

Applying the Glaze. The glaze can be put on in four ways:—1. By immersion. 2. By dusting. 3. By watering. 4. By volatilisation. The glaze is either mixed with the ingredients, or applied superficially by one of the preceding methods. Immersion. Glazing by immersion is employed in the case of porcelain, the finer Fayence ware, and sometimes for stoneware. It requires some degree of porosity in order that the glazing pap may be absorbed. The glazing materials are mixed with water to form a thin pulp. The articles previous to their immersion are slightly baked to prevent the clay being softened and running fluid in contact with the water of the glaze. The articles are dipped into the glaze, which they readily absorb, a coating or thin layer of glaze remaining on their surface when they are removed from the bath. The glaze is removed from the bottom of the article immediately in contact with the substance on which it stands to prevent its sticking. Dusting. Glazing by dusting is a surface method, and only used for costly ware. The freshly formed and still damp ware is dusted with lead glaze or minium, a layer being left on the surface. The powders employed chiefly contain oxide of lead, which combines with the silica and alumina of the clay mass during the firing to form a glaze. Recently finely-pulverised zinc blende and Glauber salt have been employed. Watering. Watering is a method of glazing employed for non-porous articles, such as English porcelain, ordinary pottery ware, and some kinds of Fayence ware. Glaze of the proper consistence is poured over the articles, the interior sometimes being left coated with a white glaze, while the outside is again coated with a coloured glaze, as is seen in common brown-ware. By Volatilisation or Smearing. Glazing by volatilisation is effected by conveying into the oven a salt or metallic vapour which shall form with the silica of the mass an efficient glaze. The most general method is applied to ware not requiring to be baked in fire-clay vessels. Common salt is placed in the oven with green wood for fuel to form an irriguous smoke. This, the salt, heated to redness, receives, and is decomposed into hydrochloric acid and soda, the vapours of which fill the oven. The inside and the outside of the vessel submitted to this process are thus simultaneously glazed. Fine stoneware baked in fire-clay vessels may be glazed by the ignition of a mixture of potash, plumbago, and common salt. During the baking or firing chloride of lead is formed, which combines with the silica of the clay to form a thin glass. This method of glazing is in England termed *smearing*, boracic acid being employed.

Lustres and Flowing Colours. A method of glazing by volatilisation, known as glazing with flowing colours, is employed for porcelain. It essentially consists in the ignition of a mixture of chloride of calcium, chloride of lead, and clay, placed in a small vessel in the firing capsule or firing chamber, and to which some metallic oxide is added, as cobalt oxide. The oxide is converted into chloride, and combines with the constituents of the article.

The Capsule, or Sagger. Porcelain ware and superfine earthenware are not exposed, when burnt, to the free action of the flame, as various impurities, such as ashes and smoke, would deteriorate the beauty. They are therefore enclosed in fire-clay vessels, termed in France *gazettes*, in Germany *kapseln*, and in England *saggers*. These saggers are manufactured of the best fire-clay, with which is mixed a cement made from broken saggers. First, into each sagger is put a perfectly true disc of the same material, and upon this the porcelain ware is placed, three knobs or small props projecting from the disc, and keeping the article from contact with a large surface to which the glaze would cause it to adhere.

Fig. 147.

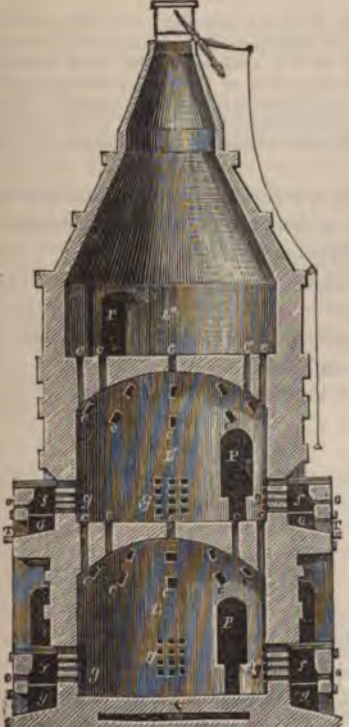
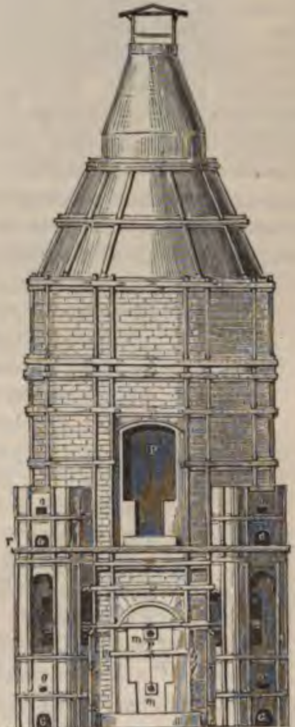


Fig. 148.



The Porcelain Oven. Fig. 147 is a vertical section of the porcelain oven, and Fig. 148 the elevation. The oven is essentially a reverberatory furnace with three stages and five fire-rooms supplied with wood fires. The oven may be considered as a tall cylinder, surmounted by a cone, in the apex of which is the chimney opening, the flat vaults by which it is divided being pierced to allow of communication. Both the stages, L and L′, serve for the "strong firing" of the porcelain. The upper stage, L″, termed variously the *howell*, *crown*, or *cowl*, serves for the "raw burning." At the bottom of both the lower stages are built the fire-places, *f*, leading by *g* into the oven. G is the ash-pit, T the opening to the ash-pit closed during the burning; *o* is an opening through which fuel is introduced; *c c* are the openings admitting of the circulation of the hot gases. P is the door by which the oven is entered. The ovens are gradually heated first to glowing heat and then to a strong red heat. At this stage the openings are closed and the oven raised to a stronger heat, at which it is allowed to remain for a short time. This intense burning lasts about seventeen to eighteen hours; the oven is then opened, and allowed to cool gradually for three to four days.

Emptying the Oven and Sorting the Ware. After the oven is cooled, the saggers containing the ware are removed, and the ware taken out. It is then separated into four kinds:—*a*. Superfine, containing no blemished ware. *b*. Medium, the ware slightly inferior in glaze, &c. *c*. The chipped and imperfectly glazed ware. *d*. Waste, or ware so distorted or cracked as to be useless.

Faulty Ware. The chief faults are:—Cracking, from the porcelain not being sufficiently plastic, from drying unequally, and from unequal heating. Part fusing from a too strong heat. Air-bubbles causing lumps to appear on the surface of the ware through the expansion of the air by heat. Spotting, from fragments of the sagger fusing and falling in upon the ware. Yellow-colouring, from smoke having entered the sagger. The chief faults in the glaze are:—Blowing, the result of the development of gas by the reaction of the constituents of the glaze upon each other; also resulting from too strong a firing. Shelling, or the exfoliating of the glaze.

Porcelain Painting. Porcelain painting is really a branch of glass painting, the colours being glass-colours, which when burnt in become durable and bright. The colours employed, technically termed mufle colours, are:—

Oxide of iron, for red, brown, violet, yellow, and sepia.
,, chromium, for green.
,, cobalt and potassium-cobalt-nitre, for blue and black.
,, uranium, for orange and black.
,, manganese, for violet, brown, and black.
,, iridium, for black.
,, titanium, for yellow.
,, antimony, for yellow.
,, copper (and protoxide), for green and **red.**
Chromate of iron, for brown.
,, lead, for yellow.
,, barium, for yellow.
Chloride of silver, for red.
Chloride of platinum, for platinising.
Purple of Cassius, for purple and rose-red.

These colours are mixed with a fluxing material, so that by the melting a silicate or borate may be formed, yielding a good glaze. Therefore the oxide of cobalt and the oxide of copper must first be mixed with silicic acid and boracic acid, oxide of antimony with oxide of lead, &c., to form a blue, green, or yellow colour, because there are few metallic oxides yielding these colours that are not affected injuriously by heat, or are by themselves sufficiently easily fluid. The burning-in of the colours is effected in a muffle, Fig. 149, the opening *o*, serving as a communication with the interior, by which the degree of heat may be ascertained; the opening, *m*, serves for the escape of the vapours of the essential oils (oil of turpentine, oil of lavender, &c.), with which the enamel colours are sometimes ground up. Fig. 150 shows the method of heating the muffle. The heating is commenced at a low temperature and is gradually increased to a red heat. From time to time the muffle is opened till the colours begin to disappear; then the muffle is carefully closed, raised to a bright red heat, and finally allowed to cool as slowly as possible.

FIG. 149.

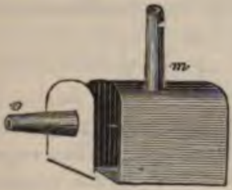
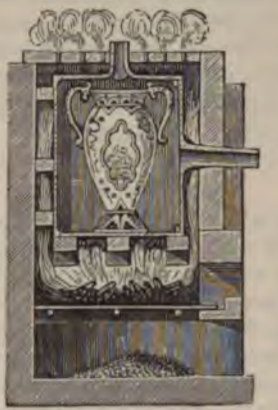


FIG. 150.



Ornamenting the Porcelain. The gold employed for decorating the porcelain is dissolved in aqua regia, and precipitated with either sulphate of iron, nitrate of protoxide of mercury, or by means of oxalic acid. In its application the gold must be intimately mixed with a flux, generally nitrate of oxide of bismuth. Shell gold is employed, also gold-beaters' refuse. The article to be gilt must be thoroughly freed from grease, else the gold will not adhere. The gold powder, finely ground up with sugar or honey, or some such soluble substance, is applied with a pencil brush. The burning-in is effected in a muffle. The gold is not melted during the burning, but becomes firmly set upon the article by means of the flux. After burning the gold does not at once appear bright, but requires burnishing with an agate tool.

Bright Gilding. Bright gilding differs from the foregoing in requiring no after polishing or burnishing. It is effected by burning-in a solution of sulphuret of gold or fulminating gold in balsam of sulphur. When an article is gilded with precipitated metallic gold or a bright gold preparation, the gilding is secure from injury by handling or scratching with the finger-nail, &c.

Silvering and Platinising. Silvering and platinising are usually only in slight requisition. Metallic silver is thrown down from its solution by means of copper or zinc; the platinum is precipitated from its neutral chloride by means of boiling with potash and sugar. The tarnishing of silver on porcelain by sulphuretted hydrogen may, according to Rousseau, be prevented by placing, before burning, a thin layer of gold upon the part silvered; the result then is a white layer of gold-silver. Much care is not necessary in this process. The silver and platinum are mixed with basic nitrate of oxide of bismuth, painted on and burnt in, and afterwards burnished.

Lithophanie. Transparent porcelain is used in the art of lithophanie, or making transparencies. A thin and unglazed porcelain plate is pressed into a flat gypsum mould bearing the pattern in high relief. The figures by transmitted light appear in delicately rounded tones of light and shade. The applications of this art to the manufacture of lamp-shades, window ornaments, &c., are too well known to need remark here.

II. TENDER PORCELAIN.

French Fritte Porcelain. Tender or fritte porcelain, is distinguished in commerce as of two manufactures—French and English. The French manufacture, in 1695, was first carried on at St. Cloud, near Paris, by Morin, who employed a glassy mass without the addition of kaolin, but containing lead, somewhat similar to crystal glass. It can, therefore, hardly be considered a porcelain, strictly so called, until melted with lime and alumina. Thus *fritte* porcelain is composed of:—1. A glass mass or *fritte*, obtained from silica and alkalies. 2. Marl, as a clay constituent. Chalk, as a lime constituent. The proportions of these constituents are:—

Fritte	75	75
Marl	17	8
Chalk	8	17

The fritte is mixed with the chalk and marl to form a thin pulp, which is allowed to remain for a month to dry, and then again pulverised. When required quickly plasticity is obtained by adding soap- or lime-water. Fritte porcelain is burnt in saggers, generally before glazing. During the burning this kind of porcelain softens more than the hard, and requires supporting on every side. It is for this reason generally baked in fire-clay moulds. The ordinary oven is employed. The glaze for tender porcelain is a kind of crystal glass containing lead. This glaze is poured over the articles, as they are non-absorbent on immersion. French porcelain is similar to cryolite glass or *hot-cast porcelain*. (See p. 291.)

English Fritte Porcelain. English tender porcelain consists of a plastic clay, so-called *China clay* or *Cornish stone*, a weathered pegmatite, with fire-clay and bone-ash. The addition of the latter is due to Mr. Spade, in 1802; recently phosphate of calcium, as apatite, phosphorite, staffelite, or sombrerite, has been substituted. The glaze is composed of Cornish stone, chalk, fire-brick, borax, and oxide of lead. The article must be baked before glazing, as the glaze is so much more easily meltible than the body of the article; and in this second firing lies the difference between the manufacture of tender and of hard porcelain. In hard porcelain the melting-point of the glaze and the body are the same. English porcelain is far less solid and more liable to crack than the hard; upon the other hand, English porcelain is the more plastic, and can be produced at a lower temperature in saggers of inferior fire-resisting qualities, consequently at a less expense. The burning takes place in a stage oven with anthracite coals, the articles being placed in saggers. The glaze is applied by immersion. Recently boracic acid has been largely employed in glazing English porcelain.

Parian and Carrara. Parian is an unglazed statue-porcelain, similar to English porcelain, but more difficultly fusible, containing less flux and more silica. The colour is a very slight yellow; the surface is wax-like. Parian was first prepared by Copeland, in 1848, although the idea was not new, as before this time Kühn, of Meissen, had prepared statues and medallions of porcelain in imitation of marble. The composition of parian is very variable; some on being tested yield phosphate of calcium, others silicate of barium, and again some contain only kaolin and felspar.

Carrara, so named in its imitation of the marble produced from Carrara in Tuscany, is intermediate to parian and stoneware, is less transparent than parian, and sometimes whiter in colour.

III. STONEWARE.

Stoneware. Stoneware differs entirely from porcelain; it is dense, sonorous, fine-grained; does not cling to the tongue. It is semi-fused and opaque. Even fine white stoneware is different from porcelain in transparency, being entirely opaque, although in some other respects similar. Stoneware is distinguished—

1. As porcelain glazed.
2. As white or coloured unglazed.
3. As common stoneware, salt-glazed.

The fine white stoneware is made from a plastic clay, burning white, and not very refractory. To the clay is added kaolin and fire-clay with a felspar mineral, generally Cornish stone, as a flux. The glaze contains oxide of lead and borax, and is transparent. The flux is used in the making of stoneware much more freely than in porcelain, in the proportion of more than half the weight of the mass. It follows that stoneware can be burnt at a lower temperature than porcelain. The articles

FIG. 151.

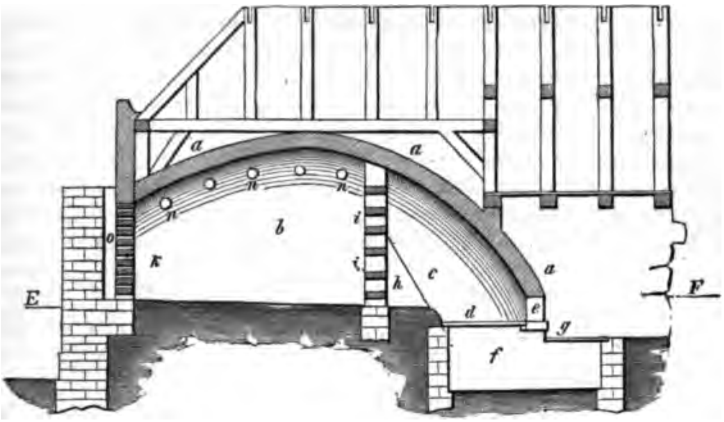
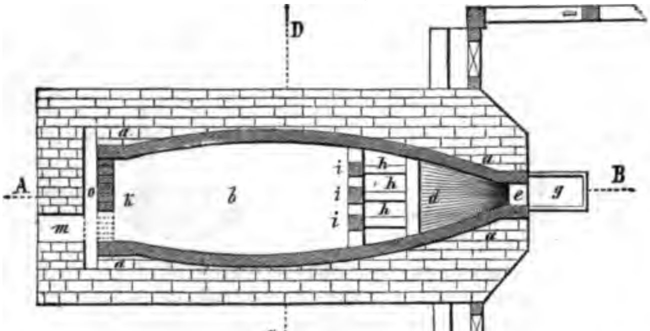


FIG. 152.



are fashioned out of the plastic clay in the same manner as porcelain. Fine stoneware is used as a cheap substitute for porcelain, it being much more easily burnt.

White or coloured unglazed stoneware, or Wedgewood ware, is made from a plastic, slightly refractory clay, kaolin, fire-clay, and Cornish stone, the latter in the proportion of half the weight of the whole. It is more easily fusible than porcelain, requiring a lower temperature in burning. The coloured stoneware is of the same composition as the white, the colouring being only superficial. Frequently other coloured clays are used for ornaments in relief. Coloured Wedgewood-ware is known as Egyptian, bamboo, fine salt ware, fine biscuit, &c.

Common stoneware differs from the preceding in containing no flux, the clay being semi-fused by the continued action of the fire. To the clay is added fine sand, or pulverised fragments of stoneware. Chemical and pharmaceutical utensils, acid tanks, &c., are made of this ware, it being strong and durable. The colour is generally grey.

Stoneware Ovens. The ovens for burning stoneware are so constructed that the articles can either lie down or be placed vertically. Fig. 151 is the vertical section of such an oven through the line A B in Fig. 152. Fig. 153 is a section through the line C D, seen from B. Fig. 154 is a section through C D, seen from A. Fig. 152 is the plan on the line E F, Fig. 151. *a a* is the arch or vault of the oven, built of clay; *b*, the vessel chamber; *c*, the fire-room; *d*, the fire-bars; *e*, the stoke-hole; *f*, the ash-pit; *g*, an air-draught; *i i*, a pierced wall; *k*, a pierced back-wall, through which the flame and hot gases escape into *o*, serving as a flue. Stone-coal is used as fuel. Another form of oven in which mineral water bottles are burnt is shown in Fig. 155. It is constructed on an easy slope; at the lowest part is the fire-room, A. In the middle of the burning-room is the pierced wall, C, technically termed the window, through which the hot gases and flame escape into D. The vault and walls, B and E, are of broken earthenware bound with mortar. A chimney is unnecessary, the gases escaping through the pierced wall, E, into the air. The burning usually takes about eight days. The high temperature at which common stoneware is burnt, and the nature of its components, render glazing unnecessary; but generally a glaze is obtained with the help of common salt placed in the oven during burning. After the

FIG. 153.

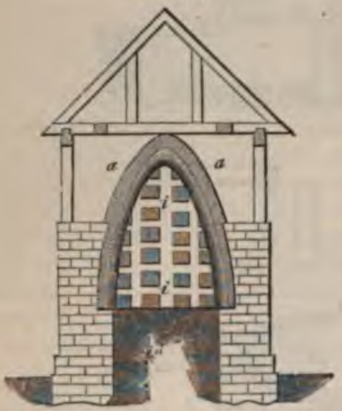
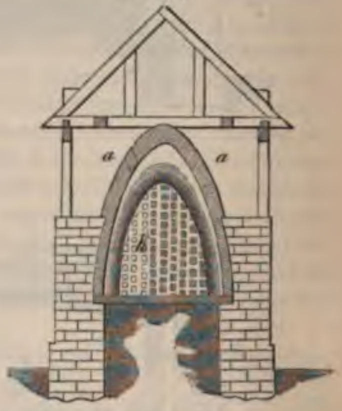
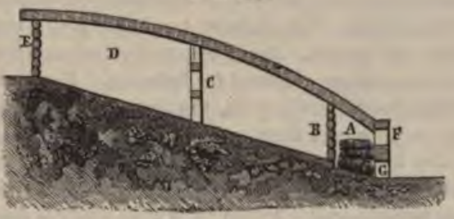


FIG. 154.



placing of the salt the openings of the oven are closed for some time, and then a second quantity of salt is introduced. The silica, with the assistance of the steam, decomposes the salt into hydrochloric acid and soda, with which it combines. Thus there is formed on the surface of the ware a glaze of silicate of soda and alumina. The salt will take up more than 50 per cent. silica, according to Leykauf's experiments; therefore, the more silica the better glaze. An oven of moderate size will require 80 to 100 pounds of salt; the purity of the salt is not a subject of much consideration. The glaze is colourless, and the vesse lappears the colour of the clay. Stoneware that is unequally coloured, one part brown, the other grey, has been brought to that state by the escape of hydrocarbons into the burning-room.

FIG. 155.



Lacquered Ware. Lacquered ware, known as Terralite and Siderolite ware in northern Bohemia, and manufactured by the firms of Villeroy and Boch, of Dresden, is an intermediate ware to fine and common stoneware; it has no glaze, but a strong surface colour of varnish or lacquer. Candlesticks, bowls, flower-vases, jugs, flower-pots, baskets, butter-dishes, fruit-dishes, &c., are formed from this ware, and baked in saggers in the usual manner. Great care and attention are required in burning the ware. The colour or bronze is mixed with varnish thinned with turpentine or linseed-oil, and applied with a pencil. The ware is then placed in a slow oven; the etherial oils volatilise, and the bronze colour becomes fixed to the surface of the ware.

IV. FAYENCE WARE.

Fayence Ware. Fayence ware (English fine stoneware) derives its name from the town of Faënza, in the Italian States, where the ware was skilfully made. In the 9th century the Spanish Moors manufactured fayence in the Island of Majorca, whence the present Majolica, the slight alteration in the manner of spelling being accounted for by Dante in his "*Tra isola di Capri e Majolica*," on the ground that the older Tuscan writers spell the name of the Island "Majolica." The industry developed from the 13th to the 15th century; from that to the 17th it culminated, and then commenced to decline. In the middle of the 16th century Bernard Palissy introduced the ware known as Palissy-fayence into France. Palissy's celebrated *Pièces rustiques* consist of ware ornamented with fish, fruit, vegetables, &c., naturally coloured in enamel. The body of porous fayence ware is earthy, and clings to the tongue. It is opaque, with more or less plasticity, and little or no sonorosity. It consists generally of plastic clay, or a mixture of this with common potter's clay. It differs from clay ware in the employment of finer materials, manipulated with greater care. Fine white fayence is distinct from common enamelled fayence. Fine fayence (semi-porcelain) consists of a plastic clay with pulverised quartz or fire-bricks, with kaolin or pegmatite and felspar minerals. It remains white after burning, and is coated with a transparent glaze. The fayence ware of different countries differ greatly; some are easily fusible, others again are burnt to a high temperature. The composition of the glaze is therefore very varied. Common lime fayence is a mixture of potter's or plastic clay, marl (clay with carbonate of lime), or quartz and quartz-sand. It is characterized by containing 15 to 25 per cent. of lime, that, at the low temperature at which common fayence is burnt, only loses a portion of its carbonic acid. The common fayence ware is thus easily distinguished from other wares by its property of effervescing when an acid is poured into a vessel made of this ware. Its fracture is earthy; the colour, consequent upon its containing 2 to 4 per cent. of oxide of iron, a decided yellow, so that an opaque glaze is employed. The glaze or enamel contains usually oxide of tin, oxide of lead, alkalies, and quartz. The more oxide of iron and lime contained in the mass, the lower the temperature required for burning. Fayence, like porcelain, is twice burnt, first without, and finally with, the glaze. It is burnt in saggers; the ware is placed in the saggers, and these are piled one upon the other in the furnace, with a layer of fat clay between each pair. The articles stand in the saggers upon small tripods in order to expose as small a contact surface as possible. The hard-burnt ware has next to be glazed. A thin pulp with water is made of the materials of the glaze placed in a cistern into which the articles are dipped. The glaze usually consists of felspar (Cornish stone), fire-clay, heavy spar, sand, borax, and boracic acid, crystal-glass, soda and nitrate of soda, white-lead, minium, and smalt. The composition of this glaze is ordinarily very complicated, but the essential constituents are silica, boracic acid, alumina, oxide of lead, and alkali. Recently the Peruvian mineral, so-called *tiza* (borate of soda and lime), has been employed. The addition of lead serves to render the glaze easily fusible, while the felspar imparts the softness characteristic of a lead-alkali glaze.

Ornamenting Fayence. Fayence is ornamented by—1. Painting; 2. Casting; 3. Printing; 4. Lustring. Painting is usually done with the brush, partly under, and partly upon the glaze. The glazing oven not attaining so high a temperature as the porcelain oven, the colours are not affected by the heat. The colours used are oxide of chromium, oxide of cobalt, oxide of iron, oxide of antimony, &c. The rose- and purple-red colours are obtained from gold preparations. The pink colour, carnation pink, was discovered in this country, and is essentially a protoxide of chromium. To make this colour—

Stannic acid	100
Chalk	34
Chromate of potash	3—4
Silica	5
Alumina	1

are well mixed and allowed to stand for some hours in a strong heat. The mass appears as a dirty rose-red colour, attaining its full brilliancy when washed with water acidulated with hydrochloric acid. The casting consists in the fayence vessel receiving a surface layer of coloured clay in any required part, independently of the colours of the mass. These coloured clays or clay-washes are made of the ordinary fat clays and metallic oxides. The printing is accomplished with the aid of a thin tissue paper, upon which the pattern is first printed from a copper plate, and afterwards transferred to the ware. For black, a mixture of forge-scale, manganese, oxide of cobalt, or chrome-black is employed; for blue, oxide of cobalt mixed with, for bright blue, fire-brick, and for less intense colours, heavy-spar, both of course being pulverised. This mixture is burnt, the frit ground, and mixed with a flux of equal parts of flint-glass and fire-clay. Copper plates, in which the pattern is deeply cut, are charged with colour mixed with linseed-oil; a transfer is then taken on the fine "pottery tissue" paper, and laid on the ware. By means of a rubber the colour is caused to leave the paper, which has been previously moistened with water, and adhere to the ware. The paper is then washed off, and the article taken to the kiln.

Flowing Colours. Flowing colours are much employed in ornamenting fayence. The common fayence or delf ware is coloured blue in this manner by means of protoxide of cobalt mixed with the glaze. When the vessels are taken to the burning-kiln, a mixture of chloride of calcium, chloride of lead, and clay is also introduced on a small plate. The protoxide of cobalt is converted into a chloride by combining with the volatilised materials, and in turn combines with components of the material of the vessel. By this means the articles obtain an apparent transparency somewhat similar to the characteristic of porcelain.

Lustres. Some kinds of ware have a second coating—a metallic lustre or glaze—given to them after burning. Gold Lustre: The different kinds of gold lustre are very similar and need not be detailed. They are essentially composed of fulminating gold and balsam of sulphur, the latter prepared by heating linseed oil and sulphur together. Platinum Lustre: This is obtained by mixing anhydrous chloride of platinum with lavender oil or balsam of sulphur; also by the well-known precipitation of platinum by sal-ammoniac. Silver Lustre is either a yellow lustre or a cantharidine lustre, so-called from its similarity in appearance to the wing-case of the Spanish fly (*Cantharis vesicatoria*). Salvétat believes that chloride of silver may be employed as a yellow lustre, similarly to gold preparations. The cantharidine lustre is generally a yellow lustre, the difference being that it is only used for white grounds, while the former is employed for blue grounds, on which it appears slightly tinged with green. Copper Lustre is both red and yellow; it is used for Spanish fayence and Majolica wares. It is chiefly formed by a silicate of copper. Oxide of lead, or lead-lustre, is merely a lead-glaze. Chloride of silver mixed with lead-lustre is reduced, the result being a deposit of a gold-yellow or a silver-white colour according to the proportion of silver.

Etruscan Vases. The vases of the old Romans were a kind of fayence ware, containing iron, and formed of a clay decomposed by quartz, only slightly burnt, sometimes unglazed, sometimes coated with an easily fusible glaze. These vases and articles are celebrated more for their beauty of form than for any peculiarity in composition, which is very analogous to the well-known delf-ware of which our table services are made.

Clay Pipes. In the manufacture of clay pipes there is employed the beautifully white pipe-clay, containing neither iron, sand, nor carbonate of lime. The clay, if pure, always burns white; but occasionally, when a yellow colour appears, the clay is burned for a longer time, whereby the oxide of iron colouring the clay is removed. The pipes are formed in a mould similar in shape to the pipe. A roll of clay is taken, and carefully spread out to the length of the pipe. The mould is constructed in two halves, hinged together like a meerschaum pipe-case, and is generally of iron. The roll of clay is placed on the lower half of the mould, and the other half is then pressed or screwed down. A wire is then pushed up the entire length of the stem. The pipe is then taken out of the mould, and set aside to dry. It is afterwards taken to the oven, where about a gross of pipes are introduced into each sagger. The saggers are long clay tubes. Sometimes the pipes are burnt without saggers. To prevent the pipe adhering to the lips on account of the porosity of the clay, the end put to the mouth is rubbed with a mixture of soap, wax, and lime-water.

Water Coolers. The Spanish water-cooling vessels, or *alcarrazas*, are made of a porous, unglazed earthenware. The constant evaporation of the water exuding to the outer surface of the vessel causes the water to be kept cool in the hottest climates. The vessels are only slightly burnt. According to Sallior, water can be cooled 15° in an alcarraza, while Sèvres ware only permits of the cooling of its contents in a similar manner some 2° or 3°. These vessels are known in France as *hydrocérames*. In this country Egyptian wine- and butter-coolers are very common, while in Egypt, Spain, Turkey, the Indies, and Americas, they are really necessaries. In Bengal these coolers are made from the mud of the Ganges. In the Levant they are termed *baldaques*; in Syria and Egypt *collies* or *gurries*, while in many places they are also known as *gargoulettes*.

V. COMMON POTTERY.

Common Pottery. To distinguish between the different kinds of this ware is extremely difficult. The manufacture is entirely distinct from the preceding. For the so-called white pottery, used for culinary purposes, ordinary potter's clay is employed, and for brown-ware a moderately refractory clay. The natural clays are, as a rule, too fat to be used without the addition of some other material, generally sand; besides sand, fire-brick, chalk, charmotte, and anthracite coal-ash. The vessels are formed upon a potter's wheel, air dried, and then glazed. The employment of a lead-glaze was but a short time ago unknown in the glazing of this kind of ware. Ordinarily the mass is white or yellow, sometimes brown-red; the glaze being transparent, the colour of the body or mass is always apparent. Partly because the ware is very easily fusible, and partly because a low heat is used in the burning, the glaze must also be very easily fusible. For this reason a lead-glaze, forming an aluminium and lead glass is very applicable, and is employed mixed with loam (clay and sand). The materials are ground and very intimately mixed in a hand-mill. The lead used is generally a lead-glance. During the burning the lead-glance is roasted, and the sulphur is driven off as sulphurous acid. The oxide of lead combines with the silica and alumina of the loam, or mixture of sand and clay, to form aluminium lead and silicate.

The glazing of the air-dried ware can be performed in three ways; either by immersion, by sprinkling, or by dusting. By immersion the workman's hands come into contact with the lead-containing glaze, with detriment both to his health and the adhering of the glaze if his hands should be greasy. This method is not therefore often employed. Sprinkling is generally adopted. In dusting, the ware is first immersed in a pulp of fat clay, and then, while still damp, dusted with the finely pulverised glaze. The danger of this process is the inhaling of the fine particles of glaze floating in the air of the workroom. When the oxide of lead is properly proportioned to the silica of the clay or loam, the resulting lead-glass is not affected by ordinary organic acids. But if the oxide of lead is not well combined with the silica, it will be dissolved by boiling vinegar. The experiments of Buchner, A. Vogel, Erlenmeyer, and others, have shown that the insolubility of lead-glaze is not so great as has been supposed, very dilute vinegar in some cases being sufficient to effect a solution. The use of vessels thus glazed may therefore have no little influence upon the health of a family, and it becomes necessary to consider if there is not some substitute. All injury likely to accrue from the use of this glaze would be removed if the potter would but re-burn imperfect ware, or employ ovens of the best construction; but this is not always the case. Recently the preparation of a glaze free from lead has been attempted, by employing water-glass, or a mixture therewith of borate of lime.

Burning. The glazed vessels are next taken to the oven. This is generally a reverberatory furnace, 2¼ to 2¾ metres in height, and 7 to 10 metres in length. At one end is the fire-grate, and at the other the chimney. The vessels are burnt without saggers, and are exposed to the full influence of the flame. The fire is at first kept low for eleven to twelve hours, and then maintained strongly for four to five hours. The vessels can be removed from the oven about eighteen to twenty-four hours after being burnt.

VI. BRICK- AND TILE-MAKING, &c.

Bricks. This manufacture may be said to include brick-making, tile-making, and the manufacture of terra-cotta goods, and must not be confounded with the ancient Egyptian method of making air-dried bricks, still pursued for some minor purposes. In order to the better comprehension of the methods of brick-making, we will first consider the preparation of the material. This may be divided into—

The preparation of the clays;
The moulding of the brick;
α. By hand.
β. By machinery;
The burning of the dried brick.

Terra-Cotta. The term terra-cotta ware generally includes the burnt, unglazed yellow or red clay ware, and also tiles, employed in building and architectural ornamentation. The preparation of this ware is almost entirely mechanical, and does not call for any further elucidation in this work than will be found in the following pages descriptive of the class of manufacture to which it belongs.

Brick Material. Various clays are used in brick-making. Usually those only are selected that will form a brick capable of bearing a considerable strain. In the burning a test-brick is employed, which is removed from time to time to see the progress of the fire, to prevent the over-burning of the bricks, or the lowering of the fire till the bricks are sufficiently burnt; but this brick must not be confounded with another test-brick for the following purpose. A brick is made of any new clay to be tested, and is set apart in an active kiln, being burnt at the same temperature as the bricks of this kiln afterwards sent into the trade. By the qualities of this test-brick the nature and worth of the new clay is judged. A batch of bricks should be composed of clays that may all be burnt at the same temperature, else very unequal results will follow; some bricks will be under-burnt and some over-burnt, while only those bricks to the clay of which the temperature is adapted will be of use commercially. A brick-clay containing much carbonate of lime can be burnt at a very low temperature, and indeed bricks so composed are very solid, and have great durability. Brick-clays often contain felspar, mica, hydrate of oxide of iron, phosphate of iron, besides organic matter. When these are not in large quantities their presence is not detrimental. Mica and felspar with oxide of iron act as fluxes, and in known quantities are useful rather than pernicious. Flint stones, large pieces of carbonate of lime and gypsum interfere with the easy applicability of brick-clays. Sulphur pyrites render clays unsuited to the manufacture of bricks, as the sulphuret of iron remaining in the brick after burning oxidises in the air to sulphate, which in a short time weathers out and renders the brick brittle. In the Netherlands, in the Thames near London, on the banks of the Ganges and Nile, in the mouths of rivers, and in nearly all clays exposed to the ebb and flow of water, is found an admirable material for brick-making. Since 1852 a mixture of lime, river sand, and water has been extensively used as a brick material, and for other building purposes.

Preparation of the Clays. The excavating of the clay for making bricks is carried on in the summer or spring. The clay is placed in not too high a layer, and allowed to weather. It is very advantageous if, during the weathering, a frost sets in. The clay is allowed to remain thus exposed to atmospheric influence until it becomes boggy or marshy. In this condition it is brought to a tank dug in the ground, 4 metres long, 2 metres broad, and 1·3 metres in depth, where it is mixed with about as much water as will stand to a height of 6 centimetres in the tank. So soon as the clay is thoroughly saturated it is treadled, that is, the brick-maker fastens boards or wooden shoes to his feet, and carefully treads over the clay, picking out all the flints, &c., which resist the passage of his foot to the bottom of the layer. This process is repeated two or three times. Sand is then added to the clay. If the clay is fat the mixture is proceeded with; but if it is a poor clay it is advantageous to wash out a portion of the sand. This may be effected in two ways. The ground-tank just described may be inundated with water, and the sand allowed to settle to the bottom; or the mixed sand and clay is placed in a large wooden tub with a hole in the side near the bottom stopped with a plug. When the water has thoroughly impregnated the clay it is let off, carrying part of the sand with it. Or the clay is stirred with the water to a thin pulp, and allowed to run out of the wooden cistern into a ground tank, where, with the water, the sand settles to the bottom. London clay, being mostly alluvial, has to be very carefully treated to free it from flint stones, &c.; it is afterwards mixed with ash or sand.

The "treading" of the clay is at the present time performed in mills, termed "pug" mills and "washers." At the late International Exhibition (1871) several machines were exhibited for performing the whole process of brick-making continuously. Among these was the three-process brick-making machine of Messrs. Clayton, Son, and Howlett, of the Atlas Works, and combining at one operation crushing, pugging, and brick-making. The rough clay is thrown into the hopper of the machine; in this hopper revolves a shaft, upon which are keyed several small knives to cut up the clay previously to its being crushed. It next passes through a pair of crushing rollers, and these effectually reduce any stones or hard lumps of clay which may enter. The clay, thus partially prepared, next passes into a horizontal pugging or mixing cylinder situated beneath, where it is mixed by the pug-knives fixed upon the central shaft. The knives force the clay towards the further end of the cylinder, where it is received by rollers and forced through the dies, forming a smooth bar of clay of the width and depth of a brick. This bar is cut into the required lengths by wires. The machine is capable of producing 20,000 to 30,000 bricks per diem, and is, perhaps, the best of its class. Mr. Bawden has constructed a machine in which no rollers or crushers are employed, the clay being turned out as wet and as soft as in hand-moulding. One horse will pug the clay and mould from 12,000 to 15,000 bricks per day. It consists of a square pug-mill, through which runs a vertical shaft bearing pug-knives. On the top of this shaft, above its bearing, is attached the horse-pole, which gives motion to the whole machine. Upon the lower end of the shaft, which passes through the bottom of the pug-mill, is a wheel having two cams, on which two rocking arms work. One arm presses the soft clay through a grating into a six-brick sanded mould, and the other arm is connected to a slide for pushing the empty sanded moulds under the grate, the empty mould at the same time pushing the full one out. Among the best Continental machines are those of Henschel of Cassel, and of Karrens.

Moulding the Brick. The moulding of the brick by hand is a very simple matter. A mould of wood or cast-iron sufficiently large to allow for the shrinkage of the material during burning is usually employed. Fig. 156 shows the plan (B), and the section (A), of the mould. Sometimes it is made so that two bricks can be moulded at the same time, Fig. 157. The moulder takes a ball of clay and places it in a sand-strewn mould, pressing it well in. Then with the striker, A, Fig. 158, he removes the superfluous clay. The mould is then emptied, and the brick placed by a child on a barrow, to be taken to some other part of the brick-field, to be sun- and air-dried. The air-dried bricks are then taken to a kiln to be burnt. In many cases the bricks are dried by artificial heat in sheds, the floors of which are heated by fires. A gang of labourers, numbering five to ten persons, can at the maximum produce only 1000 bricks per day.

Fig. 156.

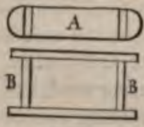


Fig. 157.

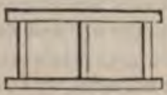
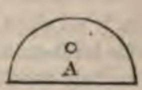


Fig. 158.



Brick Moulding by Machinery. The moulding of bricks by machinery is daily becoming more general. A moulder, no matter how experienced, has never been known to produce more than 6000 bricks in a day, and a continuity of this labour would be most improbable. Where there is a large demand, it becomes necessary to produce 30,000 bricks per day regularly, and this can be done by machinery, without employing a large number of hands. Further, the consumption of fuel in the machine can at once be stopped, or regulated to meet the demand, while a large number of workpeople cannot always be dealt with so satisfactorily to the well-meaning employer. But the machine engrosses a large capital that is not always to be invested, whereas a number of hands may be paid from the result of their labour, if the demand is good. It therefore does not always happen that machinery can compete with hand labour in this particular, as there are, in this trade especially, many makers who pay as they receive, sending out the bricks as soon as they are burnt. The machines constructed may be classed as follows:—

1. Those in which the brick is moulded or finished as by hand.
2. The machines in which the moulding proceeds uninterruptedly.
3. Those in which the brick is cut out of a cake of clay.
4. Those in which a band or stream of clay of the length and breadth of the brick is cut by means of knives or wires to the requisite depth.

I. The machines of the first class, imitating the motion of the moulder's hands, are constructed of an iron mould, with machinery or arms having a to-and-fro motion, somewhat similar to a shuttle in a loom. Such a machine is that of Carville of Issy, near Paris (Fig. 159). The brick material flows from the pug-mill, A, under the press roller, B, which is supplied with water from the reservoir, C, to prevent the clay adhering. Sand is next spread over the clay from D. The clay now arrives under the pressing apparatus worked by the arm, F, and counterpoise, G. The bricks then pass away on the endless band of moulds, I, to which motion is imparted by means of the revolving arms, J J. The bricks in the passage of the moulds over these arms are shot out, the chain of moulds passing through the tank of water, N, and thus being cleansed. M is a box to receive the waste clay, which is taken to the pug-mill. Fig. 160 is an enlarged view of the chain of moulds; M M being the plan, and the lower figure the side view.

FIG. 159.

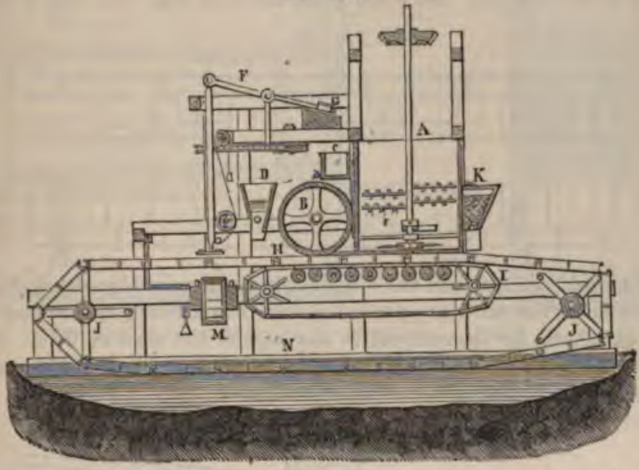
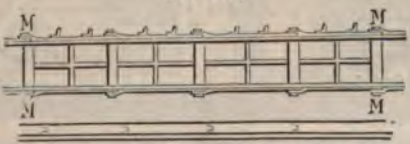


FIG. 160.



II. The second class of machines are very similar to the foregoing. Instead of the pressing apparatus, a roller is substituted, which presses the clay into the moulds as they pass under it. The moulds sometimes form the periphery of a large circle in the horizontal plane, as by this means the operation can be going on under several rollers at the same time.

III. The machines of the third class differ from the preceding in that the mould descends upon a cake of clay of the required thickness. This kind of machine is generally used in the manufacture of ornamental bricks, as by substituting other moulds any desired pattern may be produced.

IV. The machines of the fourth class, in which a band of clay is divided in cross section, may be best considered under two subdivisions, the one containing those machines in which the clay is forced through an opening of the proper size, the other those in which the clay is pressed by rollers into a band of the required dimensions. The separation is effected either by a knife or by cutting wires. By a method similar to the first process, drain pipes are manufactured. The machine of Terrasson-Fougères is a very fair example of the older system of rolling the clay. An endless band, B, conveys the clay under the press-roller, A, Fig. 161, the motion being continued by the rollers, D, and the clay kept to the required breadth by the guides, C. Fig. 162 shows the cutting apparatus mounted on a strong timber framework, G, and also on wheels for the removal to any part of the shed or field. It will be readily seen from the woodcut how the copper or iron wires kept taut by the weight, F, sever the band of clay.

Fig. 161.

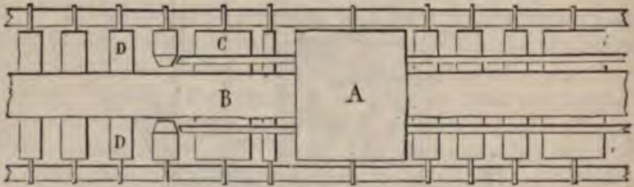
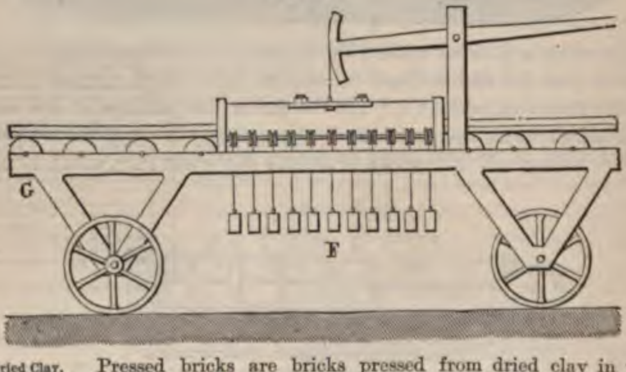


Fig. 162.



Bricks from Dried Clay. Pressed bricks are bricks pressed from dried clay in which the natural moisture of the clay is all that is employed to render the brick coherent. The pressure must, therefore, be considerably more than that used in the making of moist clay into bricks; but pressed bricks are much more solid and firm than moist clay bricks, a smaller number making a more secure wall. One of the most general machines for making this kind of brick is that of Nasmyth and Minton, in which a peculiar form of eccentric sets the moulds in action. The same movement of the primary axis pulverises the clay, and causes it to be forcibly compressed into the mould. With this machine and with that of Julienne, who has recently made some improvements, 4000 bricks can be made daily with the labour of a man and boy.

The Burning of the Bricks. The burning of the air-dried bricks or tiles is carried on in ovens or in kilns. The ovens are either open ovens, similar to a blast furnace, or vaulted, or ovens in which the burning is continuous. The fuel is partly wood, partly turf, brown coal, and anthracite or stone-coal. From the many forms of brick-kilns and ovens, the following are selected as best conveying a clear idea of the process. Fig. 163 is a stage-oven, fuelled with wood, and consisting of three chambers lying one above the other, A, B, and C. These floors can be heated in rotation. The furnace D, fed through the door, F, gives a great length of flame, which passes through the pierced wall, I, into the chamber, A, and thence through the

Fig. 163.

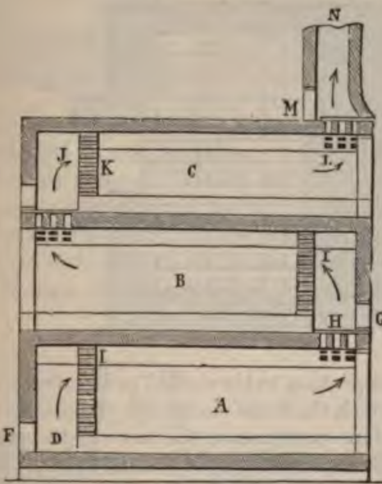


Fig. 164.

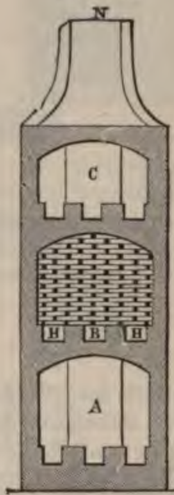


Fig. 165.

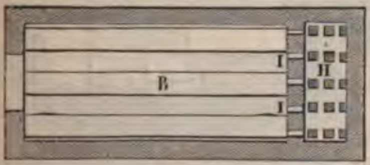
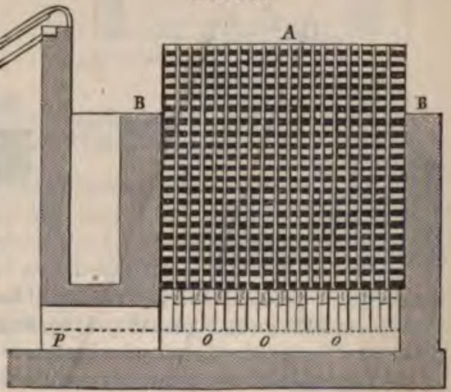


Fig. 166.



furnace, H, fed through the door, G. The flame from this hearth passes to the upper chamber, C, passing through J and the pierced wall, K, and eventually by L to the chimney, N. Fig. 164 is another section of this furnace. Fig. 165 is a plan of the middle stage. This kind of oven effects a considerable saving in fuel, as bricks can be burnt in all the stages. One of the most economical ovens burning wood fuel is shown in section in Fig. 166, and in plan in Fig. 167. There are three fire-places, of which F is the middle one. The fire-place has no grating, but is vaulted in by a series of iron bars, *o o o*, through the interstices of which the flame passes into the chamber, B B, open at the top. The bricks to be burnt are placed upon the bars *o o o* transversely, spaces being left for the passage of the flame and hot gases. It will be seen that this method of burning is much more expensive than the foregoing, owing to the amount of heat wasted; while wood as a fuel is naturally more expensive than stone-coal, to produce the same amount of heat. With the form of oven designed by Carville, and shown in Figs. 168 and 169, 80,000 bricks can be burnt with 160 hectolitres of stone-coal. Thus, as 1 hectolitre of stone-coal weighs 80 kilos., and as 100 kilos. of coal cost 3 francs 12 cents., the burning of the 80,000 bricks can be effected at a cost of 400 francs (£16). Stone-coal may be burnt in the oven shown in Fig. 170. The capacity of this oven is limited only by the enclosing walls, B B, of thick masonry. The bricks to be burnt are placed upon the sole of the oven, C,

FIG. 167.

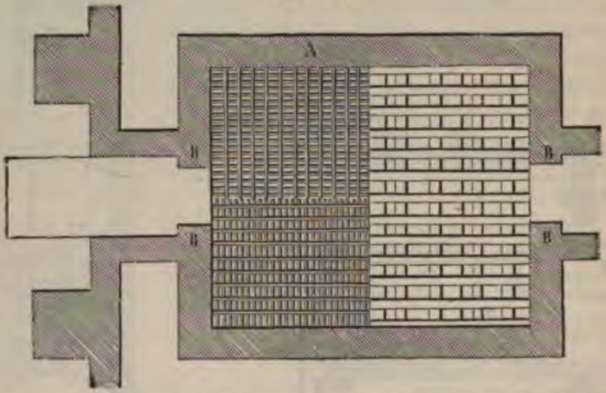


FIG. 168.

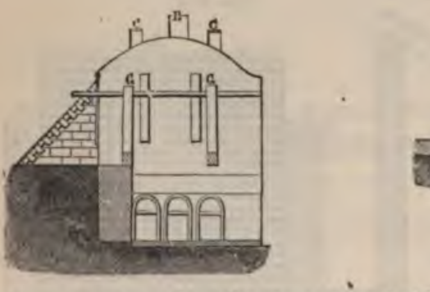
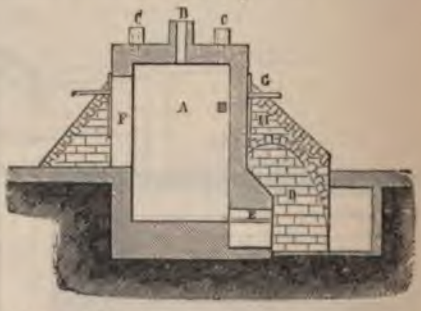


FIG. 169.



which is constructed to admit of the free circulation of the products of combustion. Fig. 171 shows the method of placing the bricks in the oven; and Fig. 172, a plan, the two hearths, D D.

Fig. 170.

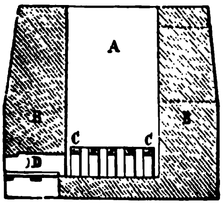


Fig. 171.

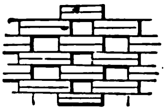
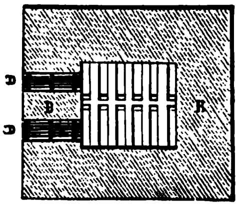


Fig. 172.



Many experiments have been made with the view of combining the burning of lime with the burning or baking of the bricks. Figs. 173 and 174 show an oven built for this purpose. The sole of the chamber, A, is covered with limestone, which is burnt equally with the bricks placed above it. The draught is regulated by the dampers in the chimney, B, and by the openings, C. The six fire-rooms are separated from each other by the blocks of strong masonry, D and G. The fuel is placed in the furnace, E, under which is the ash-pit, F.

Fig. 173.

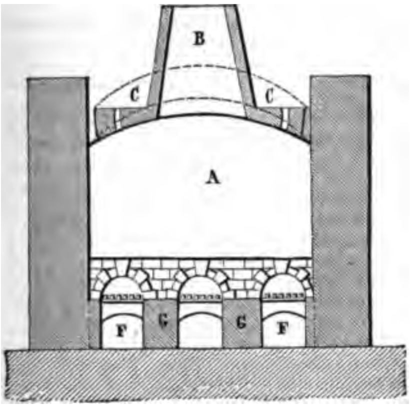
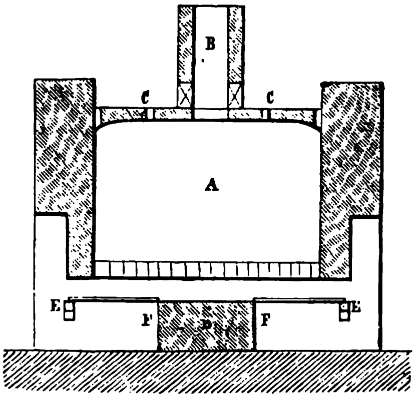


Fig. 174.



Annular Kilns. The circular or annular kilns of Hoffmann and Licht, are much used. These ovens are in plan in the form of a ring, capped by a chimney. In each oven there are a number of chambers in which the bricks are stacked. One of these chambers is filled with what are termed *green* bricks, that is bricks fresh from the field. The fire being applied, the steam passes off to the chimney. The second chamber is then filled with bricks; and when the steam has passed off from the first chamber, the products of combustion there are admitted to the second chamber through flues in the partition wall. This process is repeated with each chamber in succession. As soon as the bricks are burnt the door and flues of the chamber are opened to admit the cold air; when cold the bricks are removed, and green ones supplied in their place. It is clear that by this means there need be no interruption in the burning; and also that—

a. As the doors and flues are opened in the chamber in which the bricks have been finally burnt, the air entering is highly heated.

b. The effect being to augment the heat of the next chamber; while

c. This heat can be so proportioned out to the unburnt bricks as to render only a very short actual firing necessary.

The saving of fuel by the use of these kilns must be evident. Also from the continuity of the firing, which in practice is never allowed to go out, the ovens or chambers never get perfectly cold, and are consequently soon re-heated.

Field Burning. In contrast to the permanent kiln is the field-kiln, in which bricks or tiles are burnt at the same place that building is going on, or where a sufficiency of brick-clay is likely to yield a good return. Bricks burnt in these temporary kilns are termed *field-bricks*. The fuel employed is either turf, wood, or stone-coal. When turf or wood is used, the bricks are stacked similarly to the method employed in ovens in which these fuels are the firing materials. Flues are constructed in these kilns of the bricks themselves set in a thin layer of lime; while the wind-side of the stack is covered with hurdles thatched with straw. 50,000 bricks can thus be burnt at one firing. The flames and hot gases find their way hither and thither in the stack, and finally escape at the top. By the time that the outer bricks are hot, the interior of the stack or kiln has reached a very high temperature. When coal is employed the bricks are laid alternately with a layer of coal, a layer of lime serving as an outside cover, in which draught holes are made to regulate the burning. When the kiln is built the firing is commenced, and gradually extends to the several layers of coal until all is burnt. The kiln, consequently upon the consumption of the coal, falls or sinks together, a matter of no importance.

Dutch Clinkers. Hollanders, or Dutch clinkers, are a very hard, semi-glazed brick, of a green or dark brown colour, and possessing the property of not absorbing water.

Roofing and Dutch Tiles. For the manufacture of tiles a better and more carefully selected clay than that for ordinary bricks is employed. While "treading" is much used in the making of bricks, a mill is always considered necessary for tiles. As a rule they are burnt at the same time as bricks; the upper part of the oven being sufficiently heated for the purpose, owing to their thinness. When it is desired that the tiles should be of a grey colour, there is added to the fire, while the tiles are at a red heat, a quantity of leaves and damp twigs. By this means large volumes of smoke are disengaged, and pass into the interior of the kiln, where the pores of the tiles absorb the carbon, which imparts the grey colour remaining on cooling. Similarly the dark green colour results from the reduction of the peroxide of iron to black oxide and protoxide. Flat tiles are mostly used for paving purposes. Roofing tiles are made in many shapes; some with a nose or projecting piece, with a hole through which a nail passes to fasten the tile to the rafters; others without this protection, and with a couple of holes simply. Ridge tiles form the capping of pointed roofs and dormer windows, &c.

Drain and Gutter Tiles. The use of hollow tiles and bricks dates from a very remote period. Vaulting tiles are no more than hollow bricks or tiles, employed to reduce the weight of upper parts of large arches or masses of brickwork; they are 21 to 24 centimetres in height, and 9 to 13 centimetres in diameter, with the middle hollow and hard-burnt. A similar form of pipe is used for draining land, &c. For some purposes, bricks are constructed hollow through their width and not through the length. The advantages of hollow bricks where they are applicable are:—1. That 60 to 70 per cent. of materials are saved. 2. That they materially reduce the pressure by decreasing the weight of superincumbent masonry. 3. They dry more equally, and admit of good ventilation. 4. They can be baked at a lower temperature, with a saving of 20 to 30 per cent. of fuel. 5. The cost of transport is less consequent upon the reduced weight. Figs. 175 and 176 show two kinds of hollow tiling.

Floating Bricks. Floating bricks, or bricks sufficiently light to float upon water, are of very ancient date. Posidonius, and after him Strabo, state that a peculiarly argillaceous earth was brought from Spain, which was used to polish silver, and from which bricks could be made that would float upon water. Further, that these bricks were made in several parts of Asia, and on an island of the Tyrian Sea. Vitruvius Pollio thought these bricks to be made of a very light unknown stone; and Pliny likens it to pumice stone. But the secret remained hidden for a thousand years, until Giovanne Fabroni, in 1791, after many experiments, succeeded in producing a brick that would remain on the surface of water. The material employed was fossil meal, found near Santafiora in Tuscany. It was capable of combining with lime mortar, resisted water, and was unaltered by variation in temperature. The strength of these bricks was scarcely inferior to that of ordinary bricks, and greatly more in the proportion of their weight. Fabroni, as an experiment, constructed the powder magazine of a wooden ship of these bricks; and the vessel, being set on fire, sank before the explosion of the powder. About the same time, Faujes, of Coiron, France, found a fossil meal possessing the properties of that found in Tuscany; and in 1832, the labours of the Count de Nantes, and of Fournet, a mining engineer of Lyons, found an application for these bricks. The powder magazines, the cooking-galleys, the hearth of the steam-engine, the flues, the spirit-room on board ship can all be made of these bricks, and the chances of fire reduced. This kind of brick is also useful for the vaults of ovens, &c., in which a high temperature is maintained, as they are infusible. Kützing found that these bricks contained immense numbers of the microscopic siliceous shells of infusoria. While an ordinary brick weighs 2·70 kilos., the weight of an equal bulk of this infusoria clay is only 0·45 kilos. Coated with wax it swam like a cork. The strongest porcelain-oven-fire was without effect upon it. By the addition of clay or lime the firmness and tenacity of an ordinary brick was obtained.

FIG. 175.

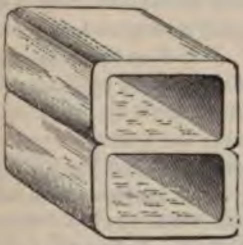
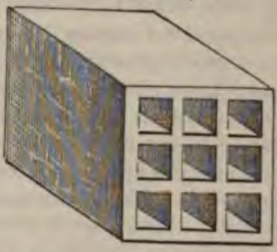


FIG. 176.



Ordinary porous bricks are made by adding to the clay, coal-dust, saw-dust, turf, tan, &c. Light bricks were used for building purposes in Nuremburg in the 14th and 15th centuries. Chimneys were built of them. In Southern Bavaria, a light brick made from a mixture of turf and sand lime has been in use for many years.

Fire-Bricks. Fire-bricks, or bricks made with fire-clay, are employed instead of ordinary bricks in the construction of furnaces, and all places exposed to an exceedingly high temperature, which would melt the common brick. These bricks contain silica and alumina, but little or no lime, protoxide of iron, or alkalies; while the clay, to prevent contraction in burning, is mixed with already burnt clay, sand, carbon (coal, coke), &c.

The process of manufacturing fire bricks at Stourbridge is so admirably described in Lieutenant Grover's "Report on Fire-clay Goods" in the International Exhibition of 1871, that the particulars may be quoted *in extenso*. "The clay," he says, "is firstly exposed in spoil heaps over as large an area as can be secured, for from 3 to 18 months, according to the state of the weather. The action of frost, as with ordinary brick earth, is of great service in disintegrating the compact tough lumps of clay, and in dry weather the clay is frequently watered. In very wet weather, a 3 months' exposure will suffice for its proper 'mellowing' or 'ripening,' and it ultimately slacks and falls to pieces. When new, it is termed, in the local phraseology, 'short and rough;' after due exposure it becomes 'mild and tough.' On some of the works the spoil heaps of clay contain over 10,000 tons, and it is estimated that 7 tons measure about 6 cubic yards. After sufficient weathering, the clay is ground in a circular pan by two rollers or cylindrical stones, shod with iron rims 2½ inches thick, and weighing from 2½ to 3¼ tons a-piece. After being ground, the clay is carried on an endless band to a 'riddle' of about 4 or 6 mesh to the inch for fire-bricks, 6 or 10 for fine cement clay, and 12 or 14 mesh to the inch for glass-house pot-clay, the larger sized mesh being used for the sifting of the clay in wet weather. The large particles which will not pass through the 'riddle' are carried back on an endless band to the pan, and there re-ground. As a general rule, it is only for very large fire-brick lumps, that re-ground pots, crucibles, or bricks—locally termed 'grogg'—are added to the clay before grinding; and fire-cement clay is always ground pure. After passing through the 'riddle' the clay is tempered, or brought to a proper degree of plasticity by the addition of water. It is then thoroughly stirred and kneaded in a circular cast-iron pug-mill, by revolving knives projecting from a vertical shaft driven by steam-power. The clay is forced down by the obliquity of the rotating knives, and streams slowly from a hole near the bottom, whence after being cut by wires into the proper forms, it travels on in an endless band to the moulding sheds. The bricks are then moulded by hand in the usual manner, and dried at a temperature of 60 or 70 degrees, in sheds about 120 feet long and 30 feet wide, beneath whose floors run longitudinally two flues. In fine weather, however, the sun's heat is made to economise fuel. The bricks are burnt in circular-domed kilns or cupolas, locally termed 'ovens,' where they remain for from eight to fourteen days, being fired with the real intensity of flame or white heat, for about four days and three nights. They usually require seven days to cool down. The fire s slowly increased and gradually lowered, the time of burning being regulated by the kilnman in charge, who inspects the baking bricks from time to time through holes in the domed roof of the 'oven.' The chimney stack is on the outside of the kiln, and the flame burns with a down draught, descending through holes in the floor, the fire-holes being merely openings left in the thickness of the wall of the kiln, and protected from the wind by buttresses long enough to allow room for the firemen to attend the fires. The coal is of course obtained from the pits which provide the clay. Most of the kilns hold each 12,000 bricks, but some are large enough to contain each 30,000 or 35,000 bricks, the capacity of a kiln being roughly calculated upon the assumption that ten bricks require one cubic foot of space in the kiln."

Some analyses of fire-clay were given when treating of the different kinds of clay. Several analyses of fire-bricks are as follows:—

	1.	2.	3.	4.	5.
Silica	63·09	88·1	88·43	69·3	77·6
Alumina	29·09	4·5	6·90	29·5	19·0
Lime	0·42	1·2	3·40	—	—
Magnesia	0·66	—	—	—	2·8
Oxide of iron	2·88	6·1	1·50	2·0	0·3
Potash	1·92	—	—	—	—
Soda	0·31	—	—	—	—
Titanic acid	2·21	—	—	—	—
	100·00	100·0	100·00	100·0	100·0

1. Clay from Dowlais. 2. Brick from copper-smelting furnace in Wales. 3. In Pembroke. 4. Brick from a blast-furnace. 5. Brick from a reverberatory furnace.

Dinas bricks are made from material obtained from the Vale of Neath, in Glamorganshire; but they have been imitated in Germany by a mixture of pure quartz-sand with 1 per cent lime. Dr. Siemens, F.R.S., says of these bricks—"Welsh Dinas brick, consisting of nearly pure silica, is the only material of those practically available on a large scale that I have found to resist the intense heat (4000° F.) at which steel-smelting furnaces are worked." Messrs. Martin Brothers, of Lee Moor, Plympton, have made some bricks from the refuse of kaolin, or china-clay, mixed with quartz-sand, carefully selected and washed. The kaolin is found in Cornwall and Devonshire, and is produced by the disintegration of pegmatite or felspathic granite, under the action of the atmosphere; it then becomes a basic silicate of alumina. The following are some analyses of these kaolinitic bricks; they possess remarkably high refractory power from the small quantity of iron contained:

Silica	75·89	75·36	73·50	76·70
Alumina	21·61	21·47	22·70	20·10
Peroxide of iron	1·96	1·79	1·70	1·70
Alkalies, waste, &c. ..	0·50	1·38	2·10	1·50
	100·00	100·00	100·00	100·00

Sanitary Ware. Sanitary ware is one of the largest branches of stoneware manufacture. Stoneware is admirably adapted for employment where an impermeable and water-tight body is desired, as in drains, sewers, subways, &c. Formerly, when about thirty years ago the manufacture of stoneware drains was commenced, the processes were all manual, and consisted in building up the large pipes or tubes section by section on a strong potter's wheel. But machinery now effects the formation of this ware with a great economy of time and labour. The clay is placed in a strong cylinder of iron, in the bottom of which is a circular opening corresponding with the solid section of the pipe; an iron piston, driven by steam, descends, forcing the clay through this opening. By this means the pipe is formed: the socket or joint is generally added on a wheel. Bends, for the turning of the corners of streets, &c., are made by simply bending the pipe by hand as it is squeezed out of the machine. Messrs. Clayton, Williams, Whitehead, and Ainslie are among the most celebrated manufacturers of these machines. Messrs. Clayton recently exhibited, at the International Exhibition, a small machine working on the principle just described, that can be manipulated by a man and a boy.

Crucibles. For crucibles it is necessary that materials shall be used that will withstand the highest temperature. Good crucibles do not crack on being rapidly cooled, and they must also withstand the action of the fluxes that may result from the smelting of metals. The most common crucibles are the Hessian, the graphite or plumbago, and the English. The Hessian crucible is made of 1 part clay (of 71 parts silica, 25 parts alumina, and 4 oxide of iron) and one-half to one-third the weight of quartz-sand. They are refractory, remain unaltered by variations in temperature, but are unsuited to some chemical operations on account of coarseness of grain and porosity. If containing too large a proportion of silica, they become perforated by oxide of lead, alkalies, &c. Graphite or plumbago crucibles are made from 1 part of refractory clay and 3 to 4 parts graphite. The Patent Plumbago Crucible Company of Battersea, as well as the Nuremberg manufacturers, employ Ceylon graphite and fire-clay. Graphite crucibles will bear the highest temperature, and they can be made to almost any required size. English crucibles are made from 2 parts of Stourbridge clay and 1 part of coke. Crucibles containing coal become reduced when heated in contact with metallic oxides, and are therefore unfitted to the smelting of metals. Recently lime and chalk crucibles have been employed for this purpose. Caron has used magnesia crucibles in the smelting of iron and steel. Gaudin employs an equal mixture of bauxite or cryolite and magnesia. Very similar are the bauxite crucibles of Audouin.

LIME AND LIME-BURNING.

Lime. Lime, protoxide of calcium ($CaO=56$), in its combination with carbonic acid as carbonate of lime ($CaCO_3$) is a substance of the most frequent occurrence. It is a constituent of bone, of the shells of the mollusca, and is found most extensively in the minerable kingdom as marble, lime-stone, coral, Iceland spar, arragonite, chalk, &c. Its technical applications are as marble in building, in the manufacture of artificial mineral waters, as Iceland spar for optical purposes, as chalk in colours and drawing materials, in the manufacture of soda, in the preparation of hydraulic mortars, building and plastering materials, &c. Limestone, Alpen lime, lias lime, Jura lime, &c., is, when mixed with clay, iron, and other metallic oxides, used as a colour. Lithographic stone is a yellow-white limestone, employed as its name implies, in lithography. Chalk or earthy carbonate of lime occurs in strata in North Germany, Denmark, France, and England. To this class belongs marl-limestone, distinguished by containing clay. With carbonate of soda, carbonate of lime forms Gay-Lussite ($CaCO_3+Na_2CO_3$); with carbonate of baryta, baryto-calcite ($CaCO_3\ \ BaCO_3$); and with carbonate of magnesia, bitter-spar or dolomite ($CaCO_3+MgCO_3$), the latter occurring with 3 molecules of carbonate of magnesia to 1 molecule of carbonate of lime.

Properties. Carbonate of lime is not soluble in pure water; but if the water should hold carbonic acid in solution, bicarbonate of lime is formed. When this solution by means of evaporation loses half its carbonic acid, an insoluble carbonate is formed. In this manner are naturally formed *stalactites* and *stalagmites*. The deposit of calc-sinter upon objects deposited in caverns, in limestone-rock, &c., is thus explained. When carbonate of lime is ignited to whiteness in a porcelain crucible, the carbonic acid is disengaged, and there remains protoxide of calcium (CaO) or caustic lime. 100 parts of carbonate of lime yield 56 parts of burnt lime. The volume of the lime undergoes no diminution by burning. Burnt lime is the form under which lime most commonly appears in the market. Carbonate of lime, heated in a closed porcelain tube, melts, and forms a crystalline mass, a carbonate, afterwards unalterable.

Lime-Burning. The burning of the lime is effected—

In kilns,
In field-ovens, and
In lime-ovens.

Lime-burning in kilns is accomplished in the following manner:—The limestone, unless it has previously been broken into small pieces, is heaped up into cairns similar to the heaps of wood to be converted into charcoal. The kiln is then covered with earth or turf, and the fire so placed that the larger pieces of lime in the interior of the heap are burnt. The regulating of the draught, the kindling, the covering, and the cooling, are on the same principle as that followed by the charcoal burner in the conversion of wood into charcoal by combustion. According to P. Löss, a kiln of this kind, 4·5 metres in height, contains 35·5 cubic metres of lime as well as 2·6 cubic metres of lime-dust. In the field-ovens the burning is similarly conducted, but sometimes on a larger scale, the kilns being always temporary. It is easy to see that the burning in this manner is only of slight technical importance; besides the great waste, only a small quantity could be produced at an operation. Therefore permanently constructed ovens are employed. These are divided into—

a. Those kilns in which the burning is interrupted, or occasionally employed (the periodical kiln).

b. Those kilns in which the burning is continuous (the continuous kiln).

In the occasional kiln, after the burning is finished, the kiln is cooled, and the lime then removed. In the continual kiln, on the contrary, the calcination is continuous, the kiln never being allowed to cool. It is so constructed that the burnt lime can be removed and fresh limestone introduced, without in the least interrupting the process. The continual kiln has many recommendations—among them that of effecting a saving in fuel, as use can be made of the refuse lime for this purpose. In a small way, where, as a rule, burning cannot be constantly carried on, the small occasional kiln is, of course, to be preferred.

Occasional, or Periodic Kilns. The occasional or periodic kiln with interrupted burnings have, or sometimes have not, a grated furnace. Figs. 177 and 178 show two lime-kilns of the ordinary construction without grated furnaces. They are built either on the slope of a hill or on the slope of the limestone quarry itself. As a rule the kilns are built near one another, so that one wall serves for two kilns. The height of the vault varies from 1·3 to 1·6 metres, and it is generally built of the largest limestones, while the smaller stones and lime-dust are placed in the interior of the kiln. Through the furnace doors, easily combustible fuel, such as brushwood, light timber, shavings, &c., is introduced. The mass becomes gradually heated, the larger stones crack and break up, and the whole mass sinks together. As the firing is increased the lime becomes of a brighter colour and the flames free from smoke. As soon as the lime immediately under the stones on the top of the kiln is at a white heat the burning is complete. The mass by this time will have sunken one-sixth. A burning generally occupies thirty-six to forty-eight hours. An occasional kiln with a grated furnace effects a quicker and more complete combustion of the fuel; but they are open to the objection that the consumption is greater. On the other hand, the kilns without a grated furnace are less perfectly heated. A kiln much used in Hanover is shown in Fig. 179, and in plan in Fig. 180; Fig. 181 shows the under part of the kiln in vertical section. The lower room serves for the calcination of the lime; over this is a vaulted chamber 3·12 metres in diameter and 11 feet in height. *e e e e*, Figs. 180

FIG. 177.

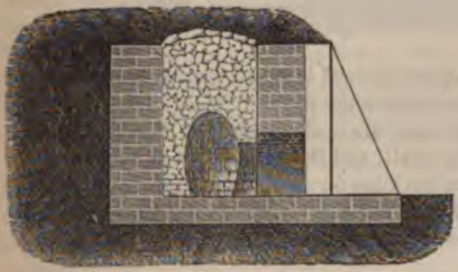
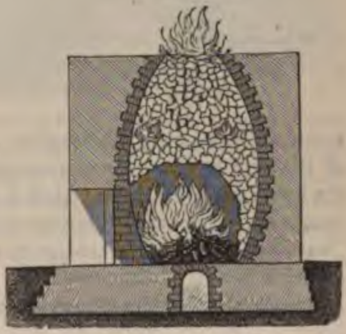
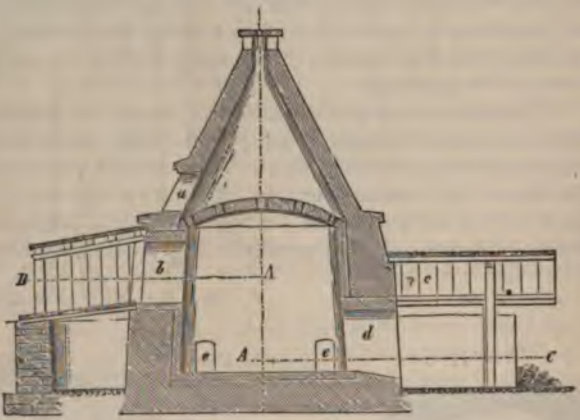


FIG. 178.



and 181, are four stoke-holes for the introduction of fuel, stone-coal, brown-coal, breeze, &c. B is the approach by which the limestone is introduced into the furnace; *d* the door by which entrance is obtained to remove the burnt lime. Both these openings are closed during the actual burning. *a* is an approach to the "upper jacket," as the upper chamber is termed. This opening is necessary as a draught to assist the flame and hot gases in their escape from the top of the kiln; it also causes a more intense flame in other parts of the kiln. Figs. 180 and 181 show how the limestone is kept clear of the hearths. A piece of wood is placed vertically in the centre of the oven to direct the flames upwards when the fire is lighted. During the first six hours the fire is weak; then a stronger fire is obtained until the yellow lime-flames spring from the openings in the vault, and the oven is in a clear glow.

FIG. 179.



The Continuous Kilns. The construction of the kilns for continuous burning is somewhat different to that of the preceding. They are of two kinds. In one the fuel and the limestone are placed in alternate layers; in the other kind, the fuel and the limestone are not in contact, there being furnaces for the former and separate chambers for the latter. In either, fresh limestone is added in proportion as the burnt stone is removed from the bottom of the kiln.

FIG. 180.

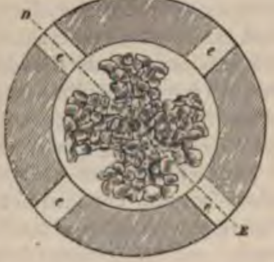
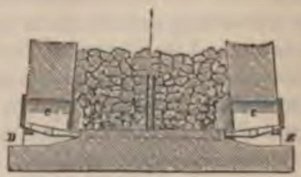
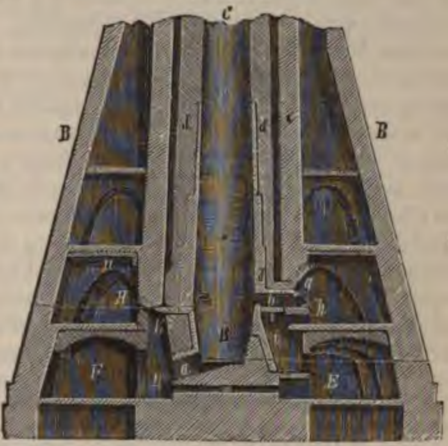


FIG.



At Rüdersdorf, near Berlin, a very efficient kiln is employed, shown in section in Fig. 182. The lining wall of the shaft, *d*, is built of fire-brick, the counter wall, *e*, is separated from the lining wall by a chamber filled with ashes, building refuse, &c. The outer wall, B B, is not an essential portion of the kiln; it serves merely as a jacket for the retention of the heat, while the galleries, H and F, can be used as drying rooms for wood, fuel, &c. During the process, the under part, B, of the shaft is filled with prepared lime, which is removed by the draught hole, *a*, in the sole of the shaft. For the purpose of hastening the descent of the burnt lime, the sides of the lower part of the shaft are sloped towards the draught-holes. The shaft is usually 14·123 metres in height. About 4 metres above the sole of the shaft is situated the fire-room, *h*. Three to five fire rooms are in action in a single shaft. The fuel is wood or turf. *i* is the ash-pit, whence the ashes fall into E. The flame enters the shaft through the opening, *b*, at the end of the fire room. The freshly-burnt lime is received in F. K K is a draught gallery communicating with H. The kilns are locally known as three-, four-, or five-fired kilns according to the number of fire rooms. Should the kiln not have been in use for some time, the firing is commenced by adding fuel, such as wood, turf, &c., to the limestone in the shaft. When the shaft is thoroughly warmed and a good draught obtained, lime only is introduced into the shaft. The shaft is entirely filled with limestone, and sometimes the limestone accumulates upon the mouth or top of the kiln to a height of 1·3 metres.

FIG. 182.



Kilns for Burning Lime and Bricks

When the locality is favourable the kilns are arranged to burn both lime and bricks at the same time. The annular kiln of Hoffmann and Licht, described under Brick-making, is the most suitable for this double purpose.

Properties of Lime.

The quality of the burnt lime is greatly influenced by the constitution of the limestone burnt. When the limestone consists chiefly of pure carbonate of lime, the resulting lime is what is termed a "fat" lime. On the other hand, if the limestone is of similar composition to dolomite ($CaCO_3 + MgCO_3$), containing magnesia, the resulting lime forms a short, thin pulp with water, and is termed "poor." With 10 per cent. of magnesia the lime is noticeably poor, and with 25 to 30 per cent. almost useless. The lime on being taken from the kiln is by no means found to be burnt equally. Some pieces that have almost escaped the fire are merely superficially burnt, and contain a kernel of unburnt limestone. Other pieces exposed to the full heat of the kiln are "over-burnt." The "over-burning" of the lime is either due to the forming of "half-burnt" lime ($CaCO_3 + CaH_2O_2$) by a strong and sudden ignition; or by means of the high temperature the small quantity of silica and alumina contained in the limestone become sintered over the surface, and the lime is thus prevented by a coating of silicate from combining with the water to form a pulp.

Slaking Lime. Burnt lime moistened with water slakes with great violence, 100 parts by weight of lime requiring only 32 parts water, or 3 vols. of lime to 1 vol. water, to obtain by the combination a temperature of 150°. The result of the slaking is a soft, white powder, lime-meal or powdered lime, hydrate of protoxide of calcium (CaH_2O_2), which in volume exceeds three times that of the lime slaked. If less water is added than is requisite for the formation of the hydrate, a sandy powder is obtained of little value technically. It is therefore very disadvantageous to place lime in baskets in damp situations. For technical application to building purposes, after the lime has been slaked with one-third of its weight of water, an equal quantity of water is added to the mass to form a thin pulp. Slaked lime retains its water of formation with such obstinacy that at a temperature of 250° to 300° no loss of weight occurs. The hydrate forms a thin pulp with water, and from this pulp by further dilution lime-water or milk of lime is obtained. If the lime-water be filtered, there results a saturated solution of hydrate of lime, containing 1 part hydrate to 778 parts water. When exposed to the atmosphere, lime-water rapidly absorbs carbonic acid, and is soon covered with a thin film of carbonate. Lime-water has a strong alkaline reaction, due partly to the lime itself, and partly to the fact that most limestones contain common salt and alkaline silicates, which, under the influence of the caustic lime, are converted into caustic alkali.

Uses of Lime. The technical applications of lime are very many. Its great affinity for carbonic acid fits it especially for the preparation of the caustic alkalies. Slaked lime is employed in the preparation of ammonia from sal-ammoniac, of hypochlorite of calcium (chloride of lime), in the precipitation of magnesia from the mother-ley of salines; in the purification of illuminating gas from carbonic acid and partly from sulphuretted hydrogen; in the refining of sugar and the separation of the sugar from beet-root juice; in the manufacture of soda; in tanning, to remove the hair and prepare the hide; in bleaching; in the manufacture of stearine candles; in the preparation of alum and sulphate of alumina from cryolite; for neutralising the sulphuric acid in the preparation of starch-sugar, &c. One of the latest applications of lime is to the oxy-hydrogen or oxy-calcium light, which is of so much importance in signalling, and such a valuable aid to the lecturer. The most important application of lime is doubtless in the making of mortar.

MORTAR.

Mortar. Mortar is a mixture of sand with cream of lime, used in building as a binding material. The ordinary mortar sets or hardens only in the air; hydraulic mortar sets under water.

a. Common or Air-setting Mortar.

When slaked lime is exposed to the atmosphere it absorbs carbonic acid, and the mass becomes much shrunken and cracked. The hydrate of lime thus formed on becoming perfectly dry attains the hardness of marble. Such a material, with certain modifications, is consequently admirably adapted as a cement to bind together bricks, blocks of stone, &c., in building. But as the contraction or shrinkage would give rise to great unevenness in the construction of walls, it becomes necessary to add sand or some similar substance to the lime-cream. This addition gives a body to the mortar, which with the bricks combines into one coherent mass. Common mortar is ordinarily made with slaked lime, an intimate mixture with sand and water being formed. Angular or sharp sand is preferred to smooth, round sand, as making a more tenacious mortar. Round-grained sand yields a very brittle mortar. The proportion of sand to the lime is a matter immediately affecting the quality and hardness of the mortar. In practice, 1 cubic metre of stiff lime-cream requires 3 to 4 cubic metres of sand; but poor, magnesia-containing lime will only admit of 1 to 2½ cubic metres of sand. When mortar is employed in brick-laying, the surface of the brick is moistened, the mortar laid between each brick, and left to dry. When dry it is often harder than the brick itself.

Hardening the Mortar. Mortar sets or hardens very quickly; after a day it will attain a firmness that will last for centuries. The drying out of the water from the mortar is not the sole cause of its hardening, as may be very easily ascertained by drying the mortar in a water-bath or over the spirit-lamp; the result is not a stone-like, but a friable, non-coherent mass. Fuchs accounts for the hardening of mortar by supposing the formation of the so-called neutral carbonate of lime ($CaCO_3 + CaH_2O_2$), a combination which has not been known to suffer conversion into ordinary carbonate of lime ($CaCO_3$). Recent researches have shown this supposition to be erroneous, as it does not agree with the results of analyses, which have yielded a quantity of carbonic acid incompatible with the existence of a neutral carbonate; 20 and even 70 per cent. of carbonic acid have been found. The experiments of Alexander Petzholdt, A. Von Schrötter, and others, have proved there to be an increase of soluble silica. The conversion of quartz-sand into soluble silica under the influence of hydrate of lime, is not, however, a reaction at all explanatory of the hardening of mortar, as washed chalk instead of silica forms an equally hard mass. W. Wolters gives the formation of silicate of lime as accounting for the hardening of mortar. It is not seldom in the analysis of old mortar from the interior of walls that caustic alkalies are found.

b. Hydraulic Mortar.

Hydraulic Mortar. Limestone containing more than 10 per cent. silica possesses, when burnt and made into a mortar, the peculiar property of hardening under water. Lime burnt from such limestone is termed *hydraulic* lime, and the mortar *hydraulic* mortar.

When unburnt, hydraulic lime is a mixture of carbonate of lime with silica or a silicate, generally silicate of alumina, the latter being insoluble in hydrochloric acid. During the burning, the hydraulic lime suffers a change similar to that taking place when a silicate insoluble in acid is precipitated, during the application of heat, with an alkaline carbonate. After burning, the lime is to a great extent soluble in hydrochloric acid, and has lost some of its carbonic acid. Von Fuchs, Feichtinger, Harms, Heldt, W. Michaëlis, and A. von Kripp's experiments have proved that the silica of hydraulic lime is precipitated in a gelatinous condition, and that constituents such as alumina and oxide of iron are of influence only when, under ignition, they have formed a chemical combination with the silica.

Hydraulic mortars are made:—

1. With a thin cream of lime and water to which sand is added; or with
2. A mixture of ordinary air-mortar with water and cement.

During the slaking of the hydraulic lime water is absorbed, but without any considerable evolution of heat or increase in volume. Hydraulic mortar is applied in the same manner as ordinary mortar—the lime-cream must be freshly made, and the brick or masonry work moistened. The mortar should be placed thickly between each layer of bricks, in order to afford a good firm bed, and allow for shrinkage.

Cements. It follows from what has been said that an artificial hydraulic mortar can be prepared from ordinary lime by the addition of silica. Such a preparation is termed a *cement*. A few natural cements are found, and may be considered as chiefly of volcanic formation. To this class belong tuff-stone, tarras, or trass, a tertiary earth, the basis of which appears to be pumice-stone with small quantities of basalt and calcined slate, the pozzolano of Italy, and santorin.

Tarras, or trass, also contains magnetic iron in small quantities, as well as titanic iron. The following are the constituents according to analysis:—

	Soluble in hydrochloric acid.	Insoluble in hydrochloric acid.
Silica	11·50	37·44
Lime	3·16	2·25
Magnesia	2·15	0·27
Potash	0·29	0·08
Soda	2·44	1·12
Alumina	17·70	1·25
Oxide of iron	11·17	0·75
Water	7·65	—
	56·86	42·98

This cement has been employed for 300 years as a hydraulic mortar, and is one of the most important of its class.

Pozzolano is another tertiary earth, occurring chiefly at Puzzuoli, near Naples, as a loose, grey, or yellow-brown mass, of partly a fine-grained and partly an earthy fracture. It contains in 100 parts:—

Silicic acid	44·5
Alumina	15·0
Lime	8·8
Magnesia	4·7
Oxide of iron	12·0
Potash Soda	5·5
Water	9·2
	100·0

The oxide of iron contains small quantities of titanium. More lime must be added to form a hydraulic mortar. The masonry of the light-room of the Eddystone Lighthouse is cemented with a hydraulic mortar formed from equal parts of pulverised pozzolano and slaked lime.

Santorin derives its name from the Greek Island of Santorin, where it was first found. It is, similarly to trass, a volcanic formation, and, according to G. Feichtinger (1870) consists of a mixture of cement and sand, the latter containing large quantities of pumice-stone. It is not largely employed as a cement, on account of the difficulty of separating the true cement from the accompanying sand.

Artificial Cements. The high price of natural cements consequent upon the smallness of the quantity found, and the difficulty of working them, has given much encouragement to the manufacture of artificial cements. Indeed, the use of natural cements is the exception and not the rule. Parker, Wyatt, and Co., were the first artificial cement manufacturers, and took out their English patent in 1796; they may therefore be considered as the founders of the extensive industry of the present day. The cement prepared by them, and now in use, is known as English or Roman cement. It is manufactured by burning a peculiar clay-shale found above the chalk formation in the Isle of Sheppey and the Isle of Wight. The burning is effected in an ordinary lime kiln, and the burnt shale is afterwards pulverised. The resulting red-brown powder eagerly absorbs carbonic acid and water from the air. It is packed in casks and stored ready for use. When prepared as a mortar, it hardens or sets in fifteen to twenty minutes.

Michaëlis found by the analysis of various Roman cements:—

	1.	2.	3.	4.
Lime	58·38	55·50	47·83	58·88
Magnesia	5·00	1·73	24·26	2·25
Silicic acid	28·83	25·00	5·80	23·66
Alumina	6·40	6·96	1·50	7·24
Oxide of iron	4·80	9·63	20·80	7·97

The analyses are from cements free from water and carbonic acid. No. 1 is Roman cement from Rüdersdorf limestone; 2. From limestone from the Isle of Sheppey, yellow-brown in colour, coarse and hard; 3. From limestone forming the under bed of the lead ores at Tarnowitz, of a blue-grey colour, firm, and of a crystalline appearance; 4. From Hausbergen limestone.

Portland cement, so named from the resemblance it bears when set to Portland stone, is a scaly crystalline powder of grey colour, and was first prepared by Mr. Joseph Aspdin of Leeds, in 1824. According to his Letters Patent, he prepared the cement in the following manner:—A large quantity of limestone was taken and pulverised; or the dust or pulverised limestone used to mend the roads was employed. This material was dried and burnt in a lime-kiln. An equal quantity by weight of clay was added to the burnt lime, and thoroughly kneaded with water to a plastic mass. This was afterwards dried, broken in pieces, and burnt in a lime-kiln to remove all the carbonic acid. The mass, thus transformed to a fine powder, is ready for the market. It is known in commerce as a grey, or green-grey, sandy, palpable powder. But Pasley must be considered the true founder of artificial cement manufacture in England; he, in 1826, obtained a cement by the burning of river-mud from the Medway, impregnated with the salts from the sea-water, with limestone or chalk. The mud from the Medway is probably best adapted for the manufacture of Portland cement on account of the sodium salts it contains, and from this supposition there seems good ground for Pettenkofer's recommendation that various marls, burnt after lixiviation with a solution of common salt, should be tried. At the present time the mud from the mouths and delta formations of several large rivers is employed in the preparation of this cement.

The manufacture of Portland cements usually follows this mode. The raw materials, limestone and clay or mud in equal quantities, are intimately mixed, the mixture dried in the air, and then burnt in a shaft-oven. The shaft-oven is generally 14 to 30 metres in height, with a width of 2·3 to 4 metres. At a height of 1 to 1·3 metres from the ground is a strong grating, through which the lumps of limestone mostly fall, those remaining being afterwards broken by the heat. The oven is so arranged that a layer of fuel and a layer of cement stone alternate. Coke is generally chosen as fuel, being found by experience best adapted for the purpose. After the mass has been submitted to a red heat for one hour, it assumes a yellow-brown colour, and at a higher temperature becomes a dark brown. Gradually the lime becomes causticised, and enters more and more into chemical combination with the silicates. At a white heat the mass becomes grey in colour, with a streak here and there of green. If during the operation these colours are shown at the several stages, the resulting cement will be good and set hard. If the heating is continued, the cement will assume a blue-grey colour and become quite useless. If removed at the first stage the mass yields a yellow-brown, light powder; at the second, a grey, sharp powder tinged with green. Beyond this stage the powder is blue-grey, or grey-white, clear and sharp, and very similar to glass-powder. The more lime the mixture contains, or, it might be said, the more basic the mixture, the more durable is the cement, and the less it falls to pieces in burning. A mixture in which clay predominates is always more or less a weaker cement, falling to pieces readily, or, technically, not binding well. According to Michaëlis, the addition of lime or alkalies prevents the cement separating, and renders it more binding; but in practice this addition would not be sufficiently economical. The more intimately the clay and lime are mixed, the larger the amount of lime that may be incorporated. From the moment of stiffening till the final hardening, the cement, if set in the air, experiences no change; but if in water, there is at first a small loss of the more soluble constituents—the alkalies.

Portland cement mixed with water to a pulp stiffens in a few minutes, and after the elapse of a day sets tolerably hard. After a month the cement sets into a substance so hard and firm that it emits a sound when struck by a hard body. It is admirably adapted, when mixed with sand or gypsum, for being cast into the various architectural ornaments, and, indeed, has from this property been termed artificial stone. Lately Grüneberg has made crystallizing-vessels of this cement, and Posch employs it in constructing reservoirs for hot fluids.

Manufacture of Artificial Cement in Germany.

The process of manufacturing true Portland cement being confined to England by letters patent, the cements of this kind made in Germany may be considered as artificial cements. They result but from a slight variation in method only, chalk and clay or mud being mixed, and the mixture formed into bricks or tiles, then burnt and ground to powder. This cement answers in every respect the purposes of the original cement. In the preparation of hydraulic mortar a mixture of chalk and lime is also used, together with marl, the ashes of pit-coal and turf, the alum-shale and alum-earth resulting from alum manufacture, burnt potter's earth, broken porcelain, pulverised flint, &c. Chalcedony cement is a mixture, invented by H. Frühling (1870), of 1 volume of burnt chalcedony with 1 volume of lime and 2 volumes of white sand. This cement has a glaze much resembling polished marble. Although the principles of the hydraulic nature of various cements and mortars are known, not many experiments have been made in verification. The elements of success seem to lie in a due regulation of the heat during burning, in the intimate mixing of the ingredients; the chief principle, the chemical combination of the several substances, is but very little known. Of the various uses of hydraulic mortars, we have nothing to do; the conditions of applicability are:—1. That the proportion of 25 per cent. of clay be preserved; 2. That the clay be of the requisite quality, rich in silica, finely divided, and form an intimate mixture with carbonate of lime. These conditions are very seldom entirely fulfilled. Portland cement was first introduced into Germany in 1850, by M. Gierow, of Stettin; and in 1852 M. H. Bleibtreu, of Stettin, erected a building at Bonn in which this cement was largely employed. Since that time there has hardly been a building in the erection of which Portland cement was not used.

M. W. Michaëlis gives the following analyses of Portland cements, the samples being free from water and carbonic acid:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Lime	59·06	62·81	61·91	60·33	61·64	61·74	55·06	57·83	55·28
Silicic acid ..	24·07	23·22	24·19	25·98	23·00	25·63	22·92	23·81	22·86
Alumina ..	6·92	5·27	7·66	7·04	6·17	6·17	8·00	9·38	9·03
Oxide of iron	3·41	2·00	2·54	2·46	2·13	0·45	5·46	5·22	6·14
Magnesia ..	0·82	1·14	1·15	0·23	—	2·24	0·77	1·35	1·64
Potash	0·73	1·27	0·77	0·94	—	0·60	1·13	0·59	0·77
Soda	0·87		0·46	0·30	—	0.40	1·70	0·71	—
Sulphate of lime	2·85	1·30	—	1·52	1·53	1·64	1·75	1·11	3·20
Clay Sand ..	1·47	2·54	1·32	1·04	1·28	1·13	2·27	—	1·08

No. 1 is Portland cement from White and Brothers, analysed by Michaëlis. No. 2 is Stettin cement, analysed by Michaëlis. Nos. 3 and 4 are Wildauer cements. No. 5, known as Star cement; and No. 6, another Stettin cement, by the same analyst. No. 7 is English cement. No. 8 cement from works near Bonn, both analysed by Hopfgartner. No. 9 is a strong and porous cement, analysed by Feichtinger.

An analytic comparison of German and English cements will be interesting. German Portland cement has the same colour as English cement, and similarly hardens under water to the same degree of durability. Under the microscope both possess the same foliated and slaty appearance. The specific weight is in both cases the same. A peculiar marl, Kufstein marl, is found in the Tyrol, near Kufstein, yielding an excellent cement, of which Feichtinger gives the following notice:—"Kufstein Portland cement is a natural hydraulic lime, unlike English Portland cement, which is an artificial hydraulic lime. It is the product of burning a marl found largely in most Alpine districts, and in every applicable condition similar to English Portland cement. The following is an analysis of this marl:—

Constituents soluble in hydrochloric acid	Carbonate of lime	70·64
	Carbonate of magnesia	1·02
	Oxide of iron	2·58
	Alumina	2·86
	Gypsum	0·34
	Water and organic substances	0·79
Total constituents soluble in hydrochloric acid		78·23
Constituents insoluble in hydrochloric acid	Silica	15·92
	Alumina	3·08
	Oxide of iron	1·40
	Potash	0·55
	Soda	0·82
Total constituents insoluble in hydrochloric acid		21·77

The quantity of the insoluble constituents amounts only to 21·77 per cent., while most marls contain much more clay; in practice, however, the clay is increased to 25 to 30 per cent. The Kufstein marl, differs, too, in the chemical composition of the clay, and as is known, the constitution of the clay greatly affects the qualities of the cements. A comparison of the two clays will therefore possess interest. In 100 parts of silica:—

	Clay from Kufstein marl.	Clay from Medway mud.
Alumina	19·34	17·0
Oxide of iron	8·79	21·6
Potash	3·45	2·8
Soda	5·15	3·0
	36·73	44·4

These analyses show, that with the clay of the Kufstein marl, a large quantity of important bases enter into combination, more than possessed by the clay of the Medway mud. Therefore the clay of this marl may be more readily smelted in a small fire. The small quantity of magnesia contained in the Kufstein Portland cement probably is productive of good effect; all good hydraulic cements contain but little magnesia."

The mention of concrete, so largely used in England where a good weathering mortar is required, must be included in that of cements. Concrete is a mixture of ordinary mortar with stones, grit, broken brick, tiles, &c. To the concrete is generally added lime, and then the whole mixed with two to three times the quantity of fine sand. Pasley tells us that a better product may be obtained with 1 part of freshly burnt lime, in pieces not larger than the fist, 3½ parts of sharp river-sand, and 1·5 parts of water, the whole being well mixed. The bricklayer prefers to mix the dry materials and then add water, the concrete in this manner taking a longer time to harden, and admitting of greater care being taken to fill all interstices. The several uses of concrete are too well known to need mention. The employment of unslaked lime in the preparation of concrete was first introduced by Mr. Smirke, of London, to whom also its employment as a foundation to brickwork is mainly due.

The Hardening of Hydraulic Mortars.

The hardening of hydraulic mortars has often been the subject of investigation. Two views may be taken: first, the mere setting, the congealing of the mass from a fluid state to a moderate degree of hardness; and then the hardening to a stony state. The knowledge we possess of the setting of these mortars is chiefly due to the experiments of Von Fuchs, Von Pettenkofer, Winkler, Feichtinger, Heldt, Lieven, Schulat-Schenko, Ad. Remete, Heereen, W. Michaëlis, and Von Schœnaich-Carolath. The cements when thus considered are best divided in two classes:—The first class, of which Roman cement is the type, embraces the mixture of caustic lime with pozzuolane, pulverised tile, and brick, and such hydraulic mortar as is obtained by burning hydraulic lime and marl. All the cements contain caustic lime unacted upon. The second class comprehends Portland cements, containing no fresh caustic lime. M. Von Fuchs has explained the chemical actions taking place during the hardening of Roman cements as being principally the combination of the lime with silicic acid, the combination giving rise to the peculiar property of hydraulic mortars. He draws this conclusion partly from the fact that from all hydraulic mortars the silica can be thrown down as an insoluble gelatinous mass by the action of carbonic acid.

A similar gelatinous mass results from the combination of silicic acid and lime. Silicates do not yield when treated with hydrochloric acid alone, gelatinous silica, but attain this property when subjected for a length of time to the influence of lime under water; the water also dissolves out the alkalies. Kuhlmann, who has long been employed in the study of the chemistry of hydraulic cements and artificial stones, states that lime can be rendered hydraulic by the intimate mixture of 10 to 12 per cent. of an alkaline silicate, or by treating with a water-glass solution. Collecting the results of these experiments, the setting of Roman cement appears due to the combination of acid silicates or silica with burnt lime, forming a hydrated silicate of lime intermixed with the alumina and oxide of iron.

The hardening of Portland cements has been investigated by Winkler and Feichtinger. According to the former, the chemical action, which is effected under the co-operation of the water, consists of the separation of the silicates into free lime and combinations between the silica and the calcium, the alumina and the calcium. The separated lime combines with the carbonic acid in the air to form carbonate of lime. The hardened Portland cement contains the same combinations as hardened Roman cement; these combinations are formed, however, under the influence of water on opposed conditions. From the results of Winkler's experiments it would appear that the silicic acid in the Portland cements can be represented by alumina and oxide of iron. Alumina does not affect the hardness, but may lessen the capability of the cement to withstand the action of carbonic acid. During the hardening the influence of the water separates the lime, till finally the combinations $Ca_3Si_3O_9$ and $CaAl_2O_4$ remain, the latter being gradually decomposed by carbonic acid, remaining, however, so long as there is any hydrate of lime in the cement. G. Feichtinger maintains a theory differing from that of Winkler. His experiments lead him to the opinion that in all hydraulic mortars the hardening depends upon the chemical combination between lime and the silica, and between lime and the silicates contained in the cement. In all hydraulic cements free lime is contained; and upon this fact we may base the following experiments. When Portland cement is brought to a pulp with a concentrated solution of carbonate of ammonia, and stirred for a long time, no hardening is traced, the greater part of the lime forming carbonate of lime. Then let the excess of carbonate of ammonia be washed away, the cement dried, and made into a mortar with pure water. This mortar will not harden unless some hydroxide of lime be added, when it hardens similarly to fresh mortar. The same result may be obtained by substituting a stream of carbonic acid gas for the carbonate of ammonia; by this means 27 per cent. of carbonate of lime may be obtained. Consequently the views of Winkler must be regarded as the most correct. These experiments also show that in Portland cements silicates or free silica are contained; that, further, free lime does and must exist. Portland cement will not take a glaze, and can only be so far affected by burning as to cause the sintering of the clay contained in the cement.

GYPSUM AND ITS PREPARATION

Occurrence. Gypsum is a hydrated sulphate of calcium according to the formula $CaSO_4 + 2H_2O$. 100 parts contain :—

Sulphur	18·60	Lime	32·56
Oxygen	27·91	Sulphuric acid	46·51
		Water	20·93
			100·00

It belongs to the commonly occurring class of minerals, and is found alone or with anhydrite (karstenite, $CaSO_4$) in strata chiefly of the tertiary formation. The following kinds are distinguished:—1. Gypsum spar, foliated gypsum, glass-stone, isinglass-stone, or selenite, possessing a very perfect cleavage, and allowing fine laminæ to be separated. 2. Fibrous gypsum, or satin spar. 3. Froth-stone, a scaly crystalline gypsum. 4. Granular gypsum, or alabaster, of coarse or fine-grained texture. 5. Gypsum stone, plaster stone, or heavy stone, a laminated gypsum. 6. Earthy gypsum, or plaster earth.

Nature of Gypsum. Gypsum is soluble in 445 parts of water at 14° C., and in 420 parts at 20·5° C.; the solubility is increased by the addition of sal-ammoniac. Its behaviour under the influence of heat is important. Graham states that gypsum placed in a vacuum over sulphuric acid and heated to 100° C., loses half its water, forming the combination $CaSO_4 + H_2O$, with 12·8 per cent. water. According to Zeidler, the statement that this combination does not harden with water is incorrect. By heating to 90° for some time 15 per cent. of the water may be expelled; at 170°, according to the experiments of Zeidler, all the water will be given off. But of more importance are the experiments not carried on *in vacuo*. In the air gypsum begins to lose its water at 100°, and the loss is not complete under 132°. Gypsum from which all the water has been removed is termed burnt gypsum, or spar-lime; it has the property of re-forming with water the same hydrate, then becoming hardened. Advantage is taken of this property in the application of gypsum as a mortar. According to Zeidler, gypsum as technically employed in stucco-work, &c., is not anhydrous, but contains 5·27 per cent. water. If gypsum is "over-burnt," that is, heated above 204°, it loses the property of hardening with water, probably owing to the fact of its being converted into anhydrite, which does not re-form with water.

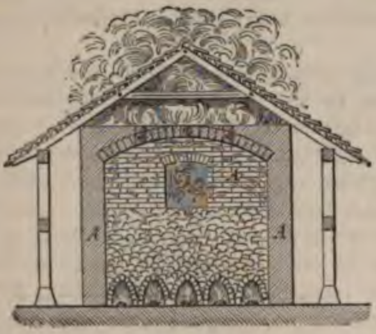
The water of crystallisation of the gypsum is saline, and consequently can be removed by the addition of salts; this probably accounts for the hardening of unburnt gypsum when treated with a dilute solution of sulphate or carbonate of potash, &c. The hardening in this follows more quickly than with burnt gypsum and pure water. With sulphate of potash a double salt is formed according to the formula $K_2SO_4 + CaSO_4 + H_2O$); gypsum and bitartrate of potash gives rise to tartar and crystalline gypsum. Chlorate and nitrate of potash, as well as sodium salts, do not effect the hardening of powdered gypsum. Gypsum thus hardened, if re-powdered and again treated with sulphate or carbonate of potash solution, hardens once more. Technical use is made of this property in re-hardening old or in hardening gypsum not sufficiently burnt, by employing instead of water a solution of carbonate of potash.

The Burning of Gypsum. Gypsum is burnt to effect the removal of the water. Lately many improvements have been made in the methods of burning, it having been found that the good qualities of the gypsum mainly depend upon the preparation. There is, however, a choice in the stone to be burnt, the heavier and denser varieties of gypsum yielding the best commercial article.

Payen, by experimenting with large quantities of gypsum, obtained the following results:—(*a*.) The lowest temperature at which the gypsum can be burnt with advantage is 80° C., a long time even then being required. (*b*.) A temperature of 110°—120° yields the best technical preparation. (*c*.) In order that the burning may take place equally, the gypsum should be first reduced to powder or small pieces. The aim, of course, is in all cases to obtain a small homogeneous product rather than a large quantity unequally burnt. Small quantities of gypsum may be burnt in an iron vessel over a coal fire: the operation should be continued till no aqueous vapour is condensed on a cold glass plate.

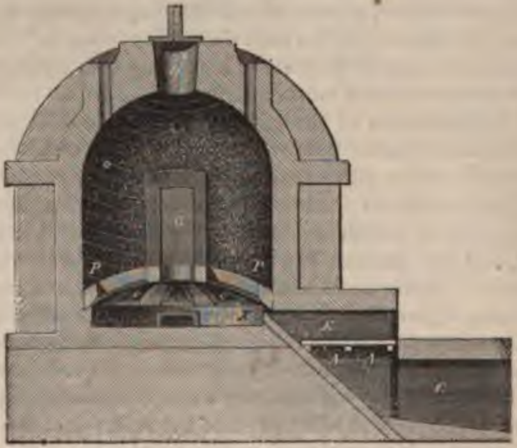
Kilns, or Burning Ovens. In large quantities gypsum is burnt in an oven or kiln, the one necessary precaution being to avoid arranging the layers of gypsum with such fuel as will reduce the gypsum to sulphuret of lime ($CaSO_4 + 4C = CaS + 4CO$).

FIG. 183.



A very simple and very general construction of kiln is shown in Fig. 183. It consists of walls of strong masonry, A, spanned by a flat arch, ventilated at *a a a*. In this room is placed the gypsum only, the fire being lighted in a series of small chambers in the lower part of the room: brushwood is the best fuel. *b* is a door through which the material is introduced. The oven (Fig. 184) used by M. Scanegatty is very similar. The inner room is divided unequally by an arch, P,

FIG. 184



about 1 foot from the floor; into the upper part the gypsum is introduced through the door G. The under part or fire-room is in connection with a flue, E, of a furnace, A A, the flames from which, driven by the draught from the gallery C, are carried through X to play upon the arch P, the hot air and gases passing through *c c c* into the upper room. The aqueous vapour escapes through H.

FIG. 185.

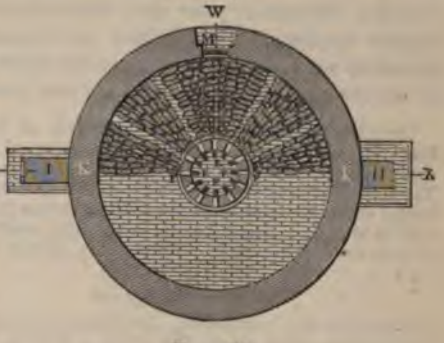
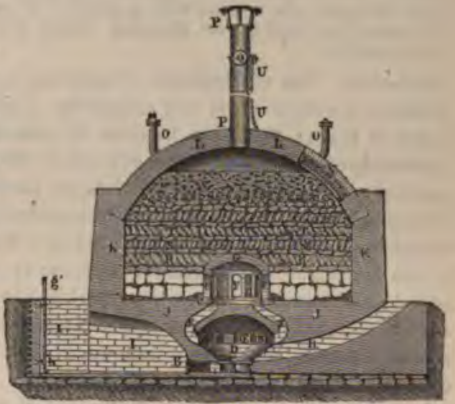


FIG. 186.



Lately Dumesnil's oven, shown in plan at Fig. 185, and in section Fig. 186, has been much employed. It somewhat resembles Scanegatty's oven in construction, and consists of an under fire-room and an upper room or oven in which the gypsum is burnt. The fire-room contains an ash-pit, A, with a door, B, a grate or grid, C, and the hearth, D. A draught, H, assists the combustion. The hot air and gases pass by the flues, E, to the chamber, F. The walls of the oven, J, K, L, are of solid masonry. I is a depth, furnished with a staircase, *g h*, to facilitate access to the furnace. P, the chimney, is of iron plate, with a clack, Q, which can be regulated by the chain U U. O O are ventilating pipes. In the wall of the burning-room are two openings; one, M, through which admittance to the interior is gained to place the lower layers of gypsum: the other, N, for the upper layers of gypsum: both are closed by doors of iron plate. An equal heat is necessary in the burning-room, and is maintained by the peculiar arrangement of the chamber F. This chamber, closed at the top by the cap, G, is provided with twelve openings, each 0·7 metre high, the chamber itself being 1 metre in diameter. The channels thus commenced by the openings in F are continued to the walls of the room by the arrangement of large blocks of gypsum. The layers of gypsum, R, S, T, are placed crosswise alternately with intermediate layers, so as to facilitate the draught in every possible way. The firing is continued gently for four hours, then strengthened for eight hours, when all the openings are closed, and five to six cubic metres of coarse gypsum powder spread equally over the top of the burning gypsum. By this means the quantity of burnt gypsum is increased without a further expenditure of fuel. After standing twelve hours in the oven to cool the whole contents are removed.

Grinding the Gypsum. After the burning the gypsum is to a certain extent in powder, but if not sufficiently even it has to be ground. The usual modes of grinding are in a stamp or roller mill. After grinding the gypsum is sifted, and placed in some position where damp cannot affect it. Sometimes the grinding and sifting are conducted in one apparatus; generally the mill and sieves are separate.

Uses of Gypsum. Gypsum is employed industrially in very many ways. It is sometimes used unburnt in building; it is then difficult to manipulate with water, but becomes soluble by continued moistening. The heavy and fast fine-grained gypsum, especially the white powdered gypsum, is used in building for architectural purposes.

From the alabaster of Voltena, Florence vases were fabricated of great beauty: the same material is used for making Roman pearls. The clear varieties of gypsum are used in the manufacture of cheap jewellery, being ground and polished. The fibrous gypsum is sometimes used for writing sand, as a substitute for pounce, &c. Fine gypsum powder is an ingredient of porcelain manufacture. Unburnt gypsum finds further application in the conversion of carbonate of ammonia into sulphate. Gypsum contains 46·5 per cent. sulphuric acid and 18·6 per cent. sulphur. It is largely employed in agriculture as a manure, both burnt and unburnt. It is generally received that the favourable action of the gypsum upon vegetation is due to the absorbed ammonia which is again yielded up.

Putridity gives rise to the formation of carbonic acid, which combines with the lime of the gypsum, leaving carbonate of lime and sulphate of ammonia. This explanation of the efficacy of gypsum-dunging, as it is termed, is, however, insufficient. The investigations of Mayer have shown that in clayey soils the oxide of iron, &c., affords larger and better combinations with ammonia than the gypsum. The quantity of gypsum used is generally about 5 cwts. to the acre, containing and realising at the most $2\frac{7}{10}$ cwts. of carbonate of ammonia. Mayer's researches, however, show that in an acre of

Field land	227 cwts.,
Chalky soil	158 cwts.,

of ammonia were contained. According to Liebig's late researches (1863) it appears that the gypsum gives up to the earth a portion of its lime in exchange for magnesia and potash. But it must be borne in mind that pulverised gypsum, as well as unburnt gypsum, when brought into contact with a solution of potash, sets into a difficultly soluble mass. We must, then, wait for an adequate theory until the several reactions have been more closely studied.

Gypsum Casts. The employment of gypsum in casting, and in all cases where impressions are required, is very extensive. A thin pulp of 1 part gypsum and $2\frac{1}{2}$ parts water is made: this pulp hardens by standing, forming ($CaSO_4 + 2H_2O$). The hardening of good, well-burnt gypsum is effected in one to two minutes, and more quickly in a moderate heat. Models are made in this substance for galvano-plastic purposes, for metallic castings, and for ground works in porcelain manufacture. The object from which the cast is to be taken is first well oiled, to prevent the adhesion of the gypsum. Where greater hardness is required a small quantity of lime is added: this addition gives a very marble-like appearance, and the mixture is much employed in architecture, being then known as gypsum-marble or stucco. The gypsum is generally mixed with lime water, to which sometimes a solution of sulphate of zinc is added. After drying, the surface is rubbed down with pumice-stone, coloured to represent marble, and polished with Tripoli and olive-oil. Artificial scaliogla work is largely composed of gypsum. Gypsum is also largely employed in the manufacture of paper.

Hardening of Gypsum. There are several methods of hardening gypsum. One of the oldest consists in mixing the burnt gypsum with lime-water or a solution of gum-arabic. Another, yielding very good results, is to mix the gypsum with a solution of 20 ounces of alum in 6 pounds of water: this plaster hardens completely in 15 to 30 minutes, and is largely used under the name of marble cement. Parian cement is gypsum hardened by means of borax, 1 part of borax being dissolved in 9 parts of water, and the gypsum treated with the solution. Still better results are obtained by the addition to this solution of 1 part of cream of tartar.

The hardening of gypsum with a water-glass solution is found difficult, and no better results are obtained than with ordinary gypsum. Fissot obtains artificial stone from gypsum by burning and immersions in water, first for half a minute, after which it is exposed to the air, and again for two to three minutes, when the block appears as a hardened stone. It would seem from this method that the augmentation in hardness is due to a new crystallisation. Hardened gypsum, treated with stearic acid or with paraffine, and polished, much resembles meerschaum: the resemblance may be increased by a colouring solution of gamboge and dragon's blood, to impart a faint red-yellow tint. The cheap artificial meerschaum pipes are manufactured by this method.

DIVISION IV.

VEGETABLE FIBRES AND THEIR TECHNICAL APPLICATION.

The Technology of Vegetable Fibre.

Vegetable fibre or cellulose, $C_6H_{10}O_5$, is the fundamental constituent of the structure of plants, forming a large proportion of the solid of every vegetable. The fibres of the hemp-plant, the nettle, and the cotton-plant are long and fluffy, and are technically termed spinning fibres. These and similar fibres are employed in fabricating woven tissues, paper, &c. Treated with sulphuric acid, cellulose is converted into dextrose or glucose. The pure cellulose constituents of wood, cotton, flax, and paper are nearly equal, as shown by the following analyses:—

Material of Cells.	Wood.	Cotton.	Flax.	Paper.
Carbon	43·87	43·30	43·63	43·87
Hydrogen	6·23	6·40	6·21	6·12
Oxygen	49·90	50·30	50·16	50·01
	100·00	100·00	100·00	100·00

The vegetable fibre for use in spinning must be firm, pliable, easily divided, and capable of withstanding bleaching operations, if required.

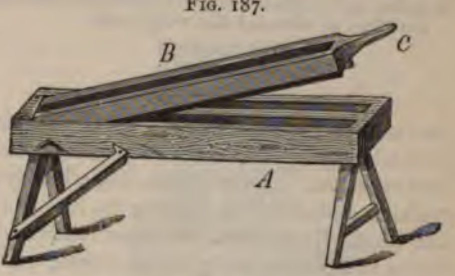
Flax.

Flax. The flax used in spinning is the fibre of the flax-plant, *Linum usitatissimum*, a plant of the class Pentandriæ, order Pentagyniæ, in the system of Linnæus, and the type of the order Linaceæ in the natural system of Botany. The flax is gathered, tied in bunches, and dried in the fields. After drying the plant is combed with an iron or flax comb, to separate the seeds, and is then bound in thick bunches. The flax fibre used in linen fabrication lies under the bark of the plant, and is surrounded by a gummy substance, or pectose according to J. Kolb, which must be removed by mechanical means to fit the fibre for industrial purposes. This is done by "softening" or "rottening," by which, according to Kolb, pectin-fermentation is set up, and the pectin converted into pectic acid. The flax is kept under water until the impurities float on the surface, leaving the fibre intact; this is the soaking method. Another method, dew-softening, as it is termed, consists in spreading out the flax in layers to the influence of the atmosphere, water being occasionally thrown over the flax. Both these methods are unsound, as the flax is liable to become rotten, while the impurities are not thoroughly removed.

Hot-water Cleansing. After many experiments with different chemical substances, an alkaline bath and dilute sulphuric acid have been found the best agents to effect the separation. The flax is placed in large vessels of water heated to 25°—30° by steam: after standing 60 or 90 hours the operation is complete. This mode of treatment, aided by an alkaline or acid solution, yields the best results, the value of the process being—1. That the construction of the fibre is equally affected, rendering the article better suited for manufacture. 2. That the fibre does not lose weight as in the other methods, where 10 per cent. is sometimes lost. 3. That there is a considerable saving in expense.

The *retted* flax, as it is technically termed, consists of cellulose and pectic acid. The next process is termed *scutching*, and includes the separating of the fibre from the woody structure of the stem. The machine for this purpose is shown in Fig. 187. It consists of two parts; the upper, B, is of wood, in the form of two splints, working on hinges. Wooden knives are placed under the splints, and are arranged to act upon the fibre placed in A by pressure upon the handle C.

FIG. 187.



Beating or Batting the Flax. Scutching consists in two operations—bruising the flax and beating away the woody part from the fibre. For the latter operation the Belgian batting-hammer, Figs. 188 and 189, is generally used. It is a deeply grooved wooden block, furnished with a long curved handle. The sheaf of flax is laid on the ground, untied, and spread out, and is beaten with the hammer by the workman. If the flax is not sufficiently loosened by batting, it is submitted to the swinging block, Fig. 190, having a cut at three-fourths of its height serving to hold about a handful of flax. This flax is then beaten with the scutch-blade, Fig. 191, a piece of hard, tough wood, generally walnut-wood. Instead of the swinging-block a grinding knife, Fig. 192, is sometimes used on an

Fig. 188.

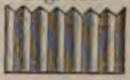


FIG. 189.

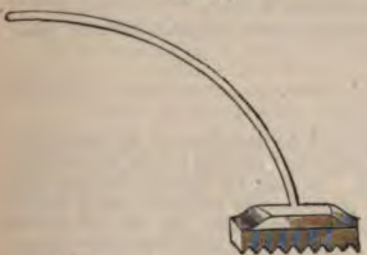


FIG. 190.

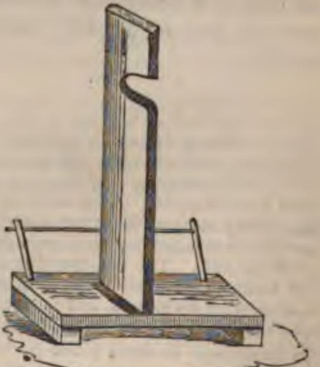


FIG. 191.

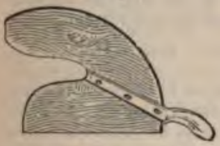
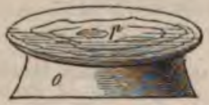


FIG. 192.



iron block. This knife is formed of a thin blade, *o*, and a heavy wooden handle, *p*. A bunch of flax is held in the left hand, at an angle for the easy use of knife with which the flax is beaten. Notwithstanding these clarifying processes the bark still adheres to the flax, which has to undergo a further operation, that of combing.

Combing the Flax. The combing or hackling of the flax removes all the material detrimental to the ultimate spinning of the fibres, and also equalises their length, rendering them smooth and parallel. The combs are made of zinc or steel, and are of varying degrees of fineness, the process commencing with a coarse comb and finishing with a fine one.

Tow, or Tangled Fibre. However carefully the operation of scutching may be performed, there is always a certain amount of waste resulting from the entanglement of the fibre, and this waste is termed scutching-tow or codilla. It is used in the manufacture of ropes, and for similar inferior purposes. The flax fibre, before it is fitted for spinning, has to be boiled in an alkaline ley, to remove the dirt and grease.

100 kilos. of cleansed flax weigh after

Bruising	45—48 kilos.
Scutching	15—25 „
Combing	10 „

Flax Spinning. The spinning of the combed flax into yarn is effected by hand and by machinery. The combed flax is first placed in bands of equal thickness, and then stretched. The hand-spinning wheel is universally known. The mechanical spinning consists in—1. Placing the fibres in a parallel series of equal thickness and length throughout. 2. These bands are stretched, the finer the fabric to be woven the greater being the stretching required. 3. By further stretching and twisting cord is spun. 4. The fine cord is still further stretched and twisted. Tow, or codilla, is spun similarly to the flax, being previously combed and placed in bands of equal length. Flax yarn is either used unbleached or is bleached before spinning. Linen thread is obtained by twisting several cords together.

Weaving the Linen Threads. By weaving the cords parallel to one another, chain cords are spun. Webbing, wrappers, and thick fabrics are made in this way.

Linen. Linen is produced by weaving the twisted cord. The selvage is made by the return of the shuttle on each side of the fabric. For coloured fabrics coloured threads are used instead of white, only more shuttles are required, one shuttle to each colour. Linen damask is woven in various patterns, as well as drill, the difference being that the woof forms the pattern on drill, while chain-cord is used for that of damask. Batiste is a fine linen cloth, slightly thinner than cambric.

HEMP.

Hemp. Hemp (*Cannabis sativa*), is chiefly cultivated for the fibre of its inner bark. This fibre, although rough, is very hard and firm, and better adapted for the manufacture of sail-cloth, canvas, rigging, &c., than any other. Its uses for inferior domestic purposes are manifold. The working of the hemp stalk accords essentially with that of flax, being steeped in water, dried and crushed in a hemp mill. By the old method the husk is crushed under a large stone cone, Fig. 193, moving in a circular course around a vertical axis. The construction of the new hemp mill, Fig. 194, is more advantageous. The hemp is purified by winnowing and afterwards combing. It is difficult to spin on account of its length, and is woven in two or three parts. Of late various foreign fibres have been used as substitutes, principally the following:—

Its Substitutes. a. *Stalk Fibre.*

1. Chinese grass (*Chinagras Tschuma*), a fibre from *Urtica s. Boehmeria nivea* and *heterophylla*, which is cultivated in China and the East Indies, Mexico, the Valley of the Mississippi, Cuba, the Waldenses in Russia, the South of France, and in Algiers. The Chinese method of treating the fibre is remarkable. The fibre is not spun, but cut into appropriately small pieces, these being placed end to end, and rolled by the hand until joined together. The fibre is thus rolled quite smooth and does not require pressing. It forms

a beautiful texture of singular brightness, called grass linen, or *China grass cloth*. The raw material is of a green or brown colour, but when bleached can, be dyed any colour.

2. The Great Nettle, *Urtica s. dioica*. The interior fibrous pith supplies the material for nettle cloth and muslin.

3. Ramie hemp, from *Urtica s. Boehmeria utilis*, is of the nettle species, and a native of Borneo, Java, Sumatra, and other islands of the Indian Archipelago. Of late various experiments as to its mode of manufacture have been tried in Germany. It is from one to two metres in length, of a delicate golden white, and not so bright and stiff as flax.

4. Rhea Grass, *Urtica s. Rhea tenacissima*, is a native of the East Indies, of little value for manufacture.

FIG. 193.

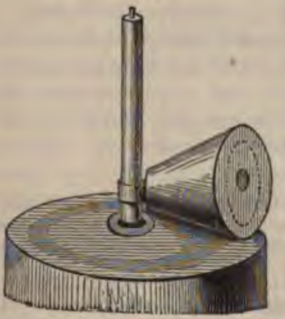
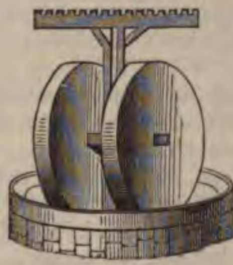


FIG. 194.



5. Jute (*paut hemp*), is obtained from a lime tree, a native of the East Indies and China, *Corchorus capsularis, C. textilis, C. olitorius, C. siliquous*. The fibre for spinning is brown, and in England is used for sackcloth and coarse packing thread. It is not a material adapted for purposes of nautical application, as it has not sufficient firmness to withstand water.

6. Bombay Hemp, from *Hibiscus cannabinus*. The woody fibre of this plant is roasted and separated by means of beating. In England it is used for cordage, rigging, &c.

7. Sun Hemp, Japan, or East Indian Hemp, from *Crotolaria juncea*, resembles other hemp in the length and firmness of its fibres.

β. *Leaf Fibre.*

8. New Zealand Flaxes (*Phormium tenax*) are used in their native country for articles of domestic use. The leaf is straight, the fibre tough, and of a shining white. The prepared material is similar to ordinary hemp in roughness and stiffness.

9. Aloe Hemp is a native of Peru, the East and West Indies, and Mexico. *A. Americana, A. Vivipara, A. Foetida*, &c., where the leaf is cultivated for its fibre, which is generally a yellow-white, and used for rope-making.

10. Manilla Hemp (Feather Fibre) comes from *Musa textilis, M. troglodytarum*, and *M. paradisiaca*, a native of the East Indies and many islands of the Indian Archipelago. It is commercially known as a yellow-white or brown-yellow fibre, from 1·3 to 2·2 metres long. The inside bark is stripped off from the bottom upwards, refined, and combed. The white kind is silky and bright, and is used in the manufacture of damask furniture and various fancy articles.

11. Ananas Hemp comes from the West Indies, Central and South America, where the common Ananas is cultivated, *Ananassa sativa s. Bromelia ananas*, as well as other species. It is rather inferior to some for spinning.

12. Pikaba Hemp is from the leaf of the *Attalia funifera*, a Brazilian palm. It is used in rope-making.

13. Cocoa-nut Fibre is a reddish-brown fibrous material, in which the cocoa-nut shell (*Cocos nucifera*) is enveloped. It is very strong and elastic, and is used for matting, ropes, hurdles, &c

COTTON.

Cotton. Cotton is the fruit of a shrubby plant of the species *Gossypium*, cultivated in the tropics and the Southern States of America for manufacturing purposes. The fruit consists of a cup-shaped calyx, enclosed in a three-cleft exterior calyx, bearing a soft white down. Another species, *Gossypium religiosum*, bears a yellow down, used by the Chinese in manufacture. The down is kept separate from the seed when packed for travelling, to prevent its becoming oily and unfit for use. While in a raw state, it is subjected to an operation termed ginning in a saw-gin, to separate the wool from the seed. Whitney's saw-gin consists of 18 to 20 circular saw-blades, revolving on a horizontal axis about 100 times a minute. The teeth of these saws project through a grating, seize the wool and pull it through, the bars of the grating being too narrow to admit the seed. Twenty saw-blades will clean 400 lbs., and 80 saw-blades worked by 2-horse power, 500 lbs., raw cotton per day. Of late the carding cylinder is sometimes used instead of the saw-gin. In America oil is largely extracted from the seed, 30 lbs. yielding about one pound of oil. The seed is also used for manure.

Species of Cotton. The quality of cotton is decided by its smoothness, and distinguished by the country from which it is imported. The various kinds are:—North American: Sea Island, or Long Georgia, Orleans, Upland, Louisiana, Alabama, Tennessee, Georgia, Virginia. South American: Fernambac, Bahia. Columbian and Peruvia. West Indian: Domingo, Bahama, Barthelemy. East Indian: Dhollerah, Surate, Manilla, Madras, Bengal. Levant: Macedonian, Smyrna. Egyptian: Mako or Jümel. Australian: Queensland. European: Spanish and Sicilian.

Cotton Spinning. Before being spun into yarn, the cotton has to be subjected to the following processes:—

1. The loosening and purifying of the raw cotton from the various impurities, such as sand, grit, &c., is accomplished by beating with the hand, or by the Wolf machine, by means of a cylinder, the surface of which is covered with sharp iron teeth. The Willow is similar to the Wolf, but it is not furnished with such sharp teeth. The fulling or rolling machine (*batteur étaleur*), and the beating machine (*batteur éplucheur*), are both employed. The beating machine loosens the cotton that was not quite opened, and allows it to fall through a grid beneath.

The Fulling or Rolling Machine (*batteur étaleur*).—The mechanism of this machine is smoother, and pulls in the cotton more quickly, working it into fibres of the consistence of flax, which are drawn over the roller and afterwards carded. A new machine has been constructed under the name of *l'Epurateur*, a step between the beating and cleaning machine, which supplies advantages not met with before. The Epurateur is preferable for the manufacture of wadding.

2. The Combing or Carding.—Before the cotton is placed in the carding machine, it is passed under a wooden roller to remove the surface thread and other small impurities which fall off. After the rolling the fibre appears like a delicate flax. The next operation is the true carding, in which two machines are used, the coarse comb, a revolving wooden drum covered with steel teeth, and the fine comb, which finishes the separation of the filaments of the fleece. The combed fleece, when it leaves the carding machine, is in the form of a loose ribbon band. It is now submitted to the doubling or lapping machine, to equalise the length of the bands, the carding process making the fleece loose and of unequal substance. Of late the fibres are separated before carding, the chief distinction being between the long fibre of Georgia (Sea Island), and the finer or silky fibres of Florett silk.

3. The Streching or Drawing.—The machine effecting this consists of sometimes two to six rollers, but usually two pairs of small rollers, over which the ribbons are drawn until they are of equal substance.

4. Roving, or unwinding the ribbon into yarn, which may be considered as the first process of spinning. The fleece is stretched 100 times finer than it was before drawing, and the more it is stretched the finer becomes the yarn for spinning. The yarn is strained loosely at first, in proportion to its length, and drawn more tightly as required. By this process yarns of various degree of fineness are easily obtained. The first drawing yields

coarse yarn, the subsequent drawings furnish the finest and most delicate yarn for spinning. If the yarn be too fine for the purpose required, as in the manufacture of coarse fabrics, several card ends, as they are technically termed, are placed together from the first drawing and formed into one ribbon; this process can be continued until the required texture is obtained.

Fine Spinning. The yarn (twist) is now rendered firmer by means of the throstle and the self-acting mule machine, which has quite superseded the Jenny. To the mule machine **Yarn.** we owe the yarn termed water-twist, which is very strong and indispensable in the manufacture of corded materials.

Cotton Fabrics. Of the different textures in which cotton is employed, we have those with parallel cords:—

a. Linen, glazed:—1. Calico, cotton and linen prints. 2. Nankeen. 3. Shirting. 4. Towelling cambric. 5. Scotch cambric. 6. Jaconet. 7. Printed calicoes. 8. Coloured textures, such as gingham, cotton barége. 9. Various transparent muslins, such as Zephyr, organdi, vapour, corded mull muslin, tulle, and gauze.

b. Cotton materials with cross cords:—1. Huckaback. 2. Cotton merino. 3. Drill. 4. Bast. 5. Satin. 6. Fustian.

c. A rough woollen stuff called beaverteen, resembling fustian, a finer moleskin.

d. Other cotton fabrics are:—1. Dimity. 2. Drill and fustian. 3. Cotton damask. 4. Pique.

e. From the same manufacture we get cotton velvet (Manchester).

Substitutes for Cotton. Substitutes for cotton are found in the black poplar (*Populus nigra*) and the aspen (*P. tremula*); the fibres of the latter are not so elastic as some of the substitutes discovered. The rush (*Juncus effusus*), the German tamarisk, and the thistle (*Agrostis*), the *Salix pentandra*, the *Zostera marina*, and the flax tree, supply material for manufacture. Some twenty years ago Chevalier Claussen endeavoured to open the filaments of flax by chemical action by steeping the fibres in a bath of 1 part sulphuric acid to 200 parts water, and then dipping it into a weak solution of carbonate of soda. By this process the flax is changed into a downy mass resembling cotton in lightness; but the method was not successful, as the firmness of the fibre was injured, and its value deteriorated in other ways.

Detecting Cotton in Linen Fabrics. There is a great difficulty in detecting cotton in linen fabrics when the fibres are closely interwoven. The old method of testing the presence of cotton in linen was by placing it under a powerful microscope, but chemical analysis presents more reliable methods. The following tests, recommended by Kindt and Lehnert, proves the existence of cotton in linen by absorption. The linen containing cotton fibre is placed in a bath of sulphuric acid of 1·83 sp. gr. for 1 to 1½ minutes. The cotton fibre is immediately absorbed, the sulphuric acid acting upon it more quickly than upon the linen; the fabric upon being dried has a curled or shrivelled appearance. Other fibres, sheep's wool, silk, and flax, are now treated chemically, and their smoothness and glossiness are attributable to chemical agency, which is found to be the greatest preservative against decay. The colour test of Elsner is useful, but not always successful, on account of the transition of the delicate colours being so instantaneous as to make it difficult to form a decision. As a colour-test there may be taken half an ounce of the root rubia tinctorum, macerated in 6 ounces of alcohol at 94 per cent. for twenty-four hours. When filtered, the tincture appears a clear brown-yellow. Pure linen fabrics immersed in it become a dull orange-red, and pure cotton yellow; the flax fibre will assume a yellow-red, and the cotton a bright yellow, the fabric appearing not uniform in colour, but streaky. When the fabric becomes so unequally streaked as to make it difficult to discern whether it be linen or cotton, the following test will prove decisive:—Place the streaky fabric in a solution of spirits of wine, and then in a weak solution of aniline red, by which it becomes coloured, and finally let it remain one to three minutes in a weak solution of sal-ammoniac; the colour of the cotton fibre will be dissipated and the linen will become a beautiful rose-red. From Elsner's first test for change of colour the method of previously colouring the linen fabric was established. Cochineal was selected for this purpose, and the linen placed in a weak solution, chloride of lime being used to prevent the colour in the linen running, while the cotton contained in the fabric changes colour immediately. Frankenstein's oil test for uncoloured fabrics can be recommended for its simplicity and excellence. The fabric is dipped in olive or rape-seed oil; it quickly becomes soaked through, and the surplus oil is removed by blotting-paper, the linen fibre becoming transparent, leaving the cotton opaque. When an unbleached fabric is tested in this manner it appears shining at first, but becomes dimmer in the parts where the cotton is present. A truer method of testing, however, is given by the magnifying glass. Böttger gives a test with potash. The linen fabric is immersed in a concentrated solution of potash; in about two minutes it becomes a deep yellow, the cotton fibre assuming a light yellow.

Stöckhardt gives a spirit test. Linen fabrics are placed in layers with lighted brandy; the linen fibre extinguishes the flame, while the cotton acts as a wick, absorbing the spirit. This experiment can be successfully used with coloured materials, with the exception of those coloured with chrome-yellow, chromate of oxide of lead. The singeing test requires the most delicate treatment. The fibre is placed in a glass vessel over the flame of the spirit-lamp until it becomes a light yellow; then by microscopic examination the cotton fibres will be found curled up, while the flax fibres are distended and clearly separated from each other. Hemp and flax act in the same manner, but do not separate so much. Nitric acid can be so applied as to leave the flax fibre unchanged in colour, while the hemp immediately becomes a pale yellow, and the New Zealand flaxes, *Phormium tenax*, a blood-red. The admixture of cotton in linen fabrics became known through O. Zimmermann, who tried the following test:—Place the fabric in a mixture of 2 parts saltpetre and 3 parts sulphuric acid for eight to ten minutes, then wash, dry, and treat with alcohol containing ether. The cotton so treated is soluble as collodion, the linen fibre is not.

Fig. 195.

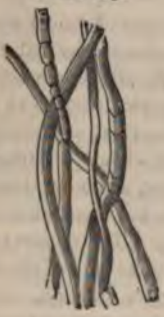


Fig. 196.

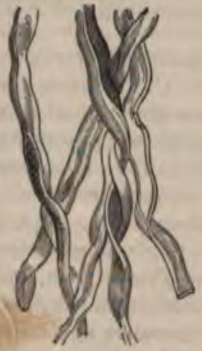
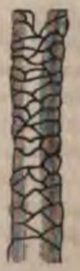


Fig. 197.



Separation of Animal and Vegetable Fibres by Means of Singeing.—The mixture is placed near a bright flame to singe until the hair is consumed, leaving a black ashy mass in the same proportion as the fibre, if it be mixed with sheep's wool.

Animal and flaxen fibres are separated by boiling in potash, which loosens the filaments of wool or silk, leaving the cotton and linen fibres unaltered. Pohl gives us the following test:—Place the fibres in a solution of picric acid for one minute; then carefully wash; the wool or silk filaments will have turned yellow, the cotton or flax fibre remaining white. This can be applied to mixed fabrics; but the most certain method is under the microscope, where the linen fibre appears in a cylindrical form, Fig. 195, and never flat. It is not stiff nor twisted, and is chiefly characterised by the narrowness of its inner tube. Hemp is similar to flax fibre, being easily broken; its ends branch out stiffly, and its tube is open. The fibres in cotton fabrics are long, of a close, thin texture, like a twisted band, as in Fig. 196. Sheep's wool under the microscope appears thicker than the other filaments, having a perfectly circular stalk with tile-shaped scales, as seen in Fig. 197. The silken fibre, Fig. 198, is a slender column, smooth on the exterior and easily distinguishable from wool, Fig. 200, representing a mixed silken and woollen fabric, as it appears under a low power. Wool and cotton, Fig. 199, are also easily distinguished from one another.

FIG. 198.

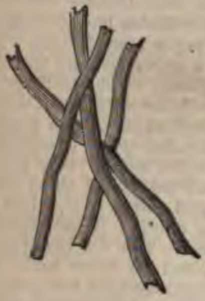


FIG. 199.

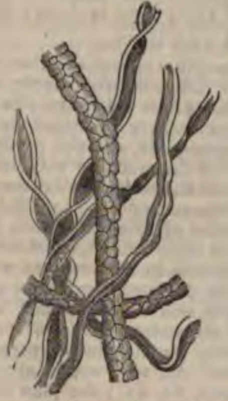
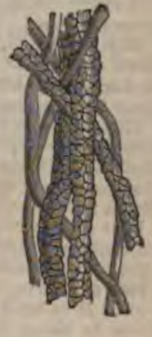


FIG. 200.



PAPER MAKING.

History of Paper. Paper is in reality a thin felt of vegetable fibres mechanically and chemically clarified, crushed and torn into a pulp suspended in water. This pulp is spread equally in thin layers, drained, pressed, and dried into the compact substance we call paper.

Of the history of paper we have the following:—In very ancient times men engraved signs upon stone, iron, lead, ivory, wood, &c., and by this means handed down their thoughts to posterity. Later, palm and other leaves were used for this purpose, also various barks of trees, especially the smooth inner bark. The old Germans wrote upon birch bark, and there is still an old Pagan poem in existence written on this bark. Other nations painted with a brush on cotton or taffeta. Indeed, about 600 years before Christ the Egyptians prepared the Cyprus grass, *Cyperus Papyrus* or *Papyrus antiquorum*, for writing purposes. This grass grew from 2 to 3 metres high; specimens are very rare. In the time of the Roman Empire it was the customary means of conveying intelligence, and was considered a luxury until 1100 or 1200, when its use was discontinued. A cotton cloth was then substituted under the name of parchment, and was held in great favour on account of its strength. Spanish paper was much esteemed until 1200. About that time an attempt was made to mix cotton with linen rags. This was accomplished in 1318. It was not well known in Germany until 1400, although the first account of its manufacture is in 1390, when Murr opened a large paper mill in Nuremburg. Later still we have mention of a paper mill by Shakspeare in the Second Part of Henry VI., the plot of the play being laid about a century before the time it was written. History records that Sir John Spielman owned a paper mill near Dartford in 1588, for the erection of which he was knighted by Queen Elizabeth. Since this time the manufacture has steadily progressed.

Materials of Paper Manufacture. The chief materials of paper manufacture are the waste rags from flax, hemp, silk, wool, and cotton. The linen rags are mostly in request for making the best and most durable white writing and printing paper. Silk and woollen rags are unfit for this purpose, as the bleaching material will not act upon animal substances. Cotton in a raw state requires less preparation than hemp. Rags are classed under different denominations,—fines, seconds, and thirds, the latter comprising fustians, corduroys, stamps, or prints as they are technically termed. The waste refuse from the wadding machine used in cotton spinning is employed for scribbling paper. Bibulous papers, such as blotting and filter papers, are made from woollen rags, on account of their open texture; cotton rags, also, make a spongier, looser paper when unmixed with linen.

Substitute for Rags. The consumption of paper in Europe has more than doubled within the last fifty years, and, owing to the inefficient supply of rags, substitutes had to be found in straw and wood. The Chinese first used vegetable pulp for paper manufacture. The inner bark of the bamboo is particularly celebrated as affording a paper yielding the most delicate impressions from copper-plate, and this paper was originally called India-proof. The Chinese also use the bark of the mulberry and elm trees, hemp, rice-straw, and wheat. Among the straw species appears the maize (Indian corn), from the fibre of which a paper is made that for purity and whiteness cannot be equalled. Also the *Andropogon glycichylum*, or *Sorghum saccharatum*, a native of North America, is used; in fact nearly every species of tough fibrous vegetable, and even animal, substance has been tried, but of these straw has been most successfully applied, in combination with linen and cotton rags, when the silica contained in the straw is destroyed by means of a strong alkali. If the straw is not properly prepared the paper will be brittle, and unfit for use. The use of straw is not very extensive, owing to the extra expense of preparation, and its waste under the process. It is used for making common brown paper, but it is chiefly used for giving a stiffness to cheap newspapers. All soft woods are fit for paper-making, such as the trembling poplar, linden, aspen, fir, &c.; the pine is of too resinous a nature to be of much value. The preparation from wood is made in the following manner:—The bark is sawn and split into suitably-sized pieces, and the fibres separated by pressure between horizontal rollers copiously supplied with a stream of water. The water, which forms two-thirds of the mass, is then removed by further pressure, generally hydraulic. In 1867, Bashet and Machard treated the woody material with hydrochloric acid. Later, waste wood has been treated chemically, in the large manufactory of Manayunk, of Philadelphia. The finest wood is set apart into lots. No. 1 is used for making writing and printing paper; No. 2, wall paper, packing paper, and inferior kinds of printing paper; Nos. 3 and 4 for label and pasting paper. Spanish woods are largely used, on account of their smoothness.

Mineral Additions to the Rags. We find minerals used in the present manufacture. A moderate addition of a mineral body to the paper material whitens the whole, and for inferior or ordinary paper is successfully employed. It is unfit for very thin paper, making it shiny and brittle. A profitable addition of mineral matter is from 5 to 10 per cent. of the weight of paper, a greater addition making the paper dull, brittle, and hairy to write upon. The usual mineral mixtures in frequent use at the present day are—clay free from sand, China clay, and kaolin. Aniline pearl-hardening, dissolved into a pulp resembling clay, is most preferred, being not so expensive. In 1850 it was favourably received, under the names of fixed white, raw white, patent white, or permanent white. With 100 kilos. of paper pulp 15 kilos. of the paste is generally employed.

Manufacture of Paper by Hand. The old method of making paper by hand was from the pulp of waste paper placed in a mould of the required size; but this method, although still used for writing paper, was found to restrict the size of the sheets, and different methods were tried with varied success, until a machine was invented which, without the aid of moulds, manufactured the paper in any length.

Cutting and Cleaning the Rags. The Cutting and Sorting of the Rags. The first operation is performed by two machines, called the half-hollander and the whole-hollander. The rags are next treated chemically with potash to rot them. By the old method, rags were cut into pieces about 4 inches square, by being drawn across a sharp knife fixed upon a table. Machinery has superseded this arrangement, and various cutting machines have been invented, among which we may mention that of Mr. Davey, in which a horizontal knife revolves around a fixed cylinder cutting the rags into strips. Bennet's cutting machine consists of two knives radiating from a wheel, and bearing against another knife. Some machines are constructed with a quantity of circular sharp-edged steel plates, like the machine of Uffenheimer, of Vienna. After cutting, the rags are cleansed from dust and other impurities by the Willow machine. The best kind of sifting machine is in the form of a drum with the upper part covered with a wire grating. The rags are put in by a side door, which acts, as the drum revolves, as a refuse door, casting off the sand and impurities, leaving the rags winnowed. They are next boiled in an alkaline ley, or solution of 4 to 10 pounds of carbonate of soda, with one-third of quick-lime to 100 of the material. The rags are placed in large cylinders slowly revolving, and causing them to be constantly turned over. Into these cylinders a jet of chlorine water, with a pressure of 30 lbs. to the square inch, is directed. H. Volter patented in 1859 a horizontal steam cylinder, which receives the steam from a tubular guide-cock provided to the boiler, an inner cylinder revolving to move the rags. The distant end of the boiler and the tubular cylinder draws up, and the mass is easily poured into the washing machine when in a fluid state (Silberman's Washing Hollander). Although partly cleansed by the above method the rags still require further boiling.

The Separation of the Rags for Half-stuff and the Whole-stuff. The machine used in separating and rending the rags are:—

1. The German stamping machine.
2. The rag mill (rolling hollander).
   - a. The half-hollander.
   - β. The whole-hollander.

Formerly the rags were rotted before crushing, being placed in a stone trough, where in two or three days they became heated, and developed a strong ammoniacal odour. When the surface was covered with a mould, the rags were sufficiently decayed for the purpose of manufacture. They were then taken out in a brown mass, those remaining behind as sediment being used for coarse paper. The present method of boiling the rags with alkalies is preferable, giving the paper greater firmness.

Stamp Machine. The German stamp machine is at the present time only to be found in smaller manufactories. It is of the nature of a hammer. Six or eight stamp rods are fixed into a strong oak beam, and work intermittently with a set below. Through an opening provided with a fine sieve the water is conveyed away. As the hammers rise and fall, the stamp holes serve for a water conduit. Three to five hammers work in each hole. The rags are mixed with sufficient water to form a pulp, and remain in the machine 12 to 20 hours and more.

The Hollander. The hollander mill is fast becoming a universal favourite. It is somewhat similar in principle to the stamping machine, but in strength and speed greatly excels every other machine. Fig. 201 is a half-hollander; Fig. 202 the vertical section through the line A B. The chief characteristics of the hollander are:—1. Speed of revolution of the trimming knife. 2. The box of knife edges under the revolving cylinder. 3. The trough and revolving cylinder. 4. The cap or partition above the trough to prevent the mass being cast out when in motion. The trough, C C, is a long oblong cistern of cast-iron, stone, or wood lined with lead. The cover rests upon a partition, *x x*, of equal height with the outside wall. The machine is divided into two parts, the working side in which the rags are torn or shredded between the knife-edges on the cylinder and those in the box, and the running side into which the shredded rags are thrown by the revolving cylinder. Under the cylinder is a massive oak block, *t*, the craw, its concave surface comprising the fourth part of the circumference of the cylinder. The side *y* is a little, and *z* much inclined. Half-way between *h i* are two strong beams, *l*, *m*, supporting the metal bearings, in which works the axle, *o o*, of the cylinder. From the roller, Q, a numbers of cutters run parallel to the axis. The knives are of soft steel, and in the whole-hollander sometimes bronze. Beneath these a series of knives is placed, against which the rags are drawn by the cylinder. In order that by the movement of the cylinder none of the material should be thrown out, a cover is provided, the dirty water thrown up falling through the sieves, *v v*, and flowing through the opening, *g g*. Clean water flows in from the top of the hollander. The washing finished, the water pipe is shut by means of a sliding partition, each partition having an inner one to prevent the pulp passing away. The rags are poured into the top of the hollander with the requisite quantity of water. The roller revolves 100 to 150 times a minute, the

FIG. 201.

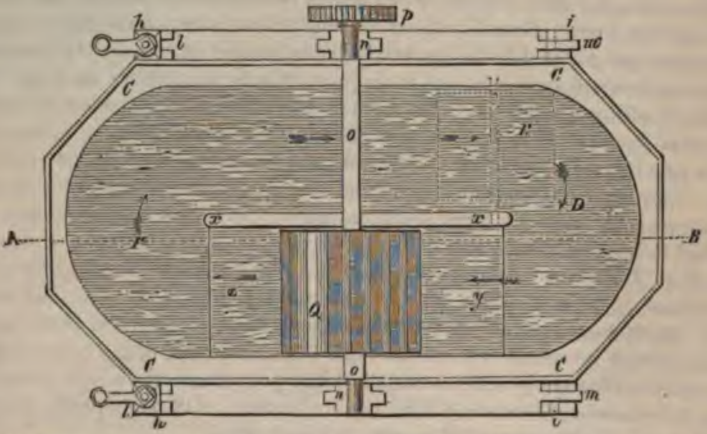
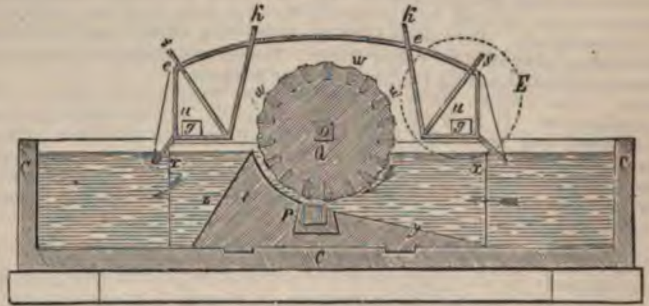


FIG. 202.

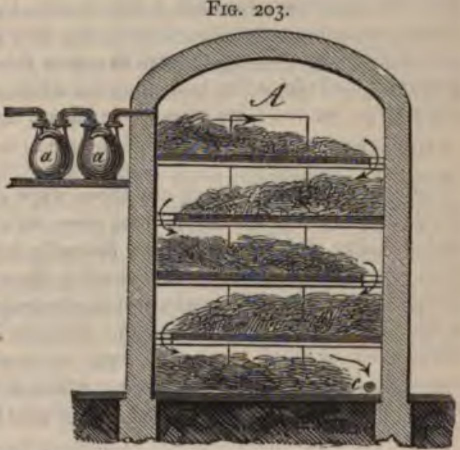


knives cutting more readily in the fluid. Having passed the cylinders and the lower set of knives, the mass flows over the steep slope of the craw, *z*, while the roller continues its work. This mode has this advantage, that the rags have an uninterrupted flow, and that all parts have the same resistance under the roller. The work of the half-hollander is of two hours duration for soft and clean rags, a longer time being requisite for coarse and dirty materials.

Bleaching the Pulp. After this the mass is placed in another machine, the whole-hollander, and bleached by a solution of chloride of lime, chlorine water, chlorine gas, or other bleaching agents. The lime is retained in the machine until the rags are sufficiently bleached; the pulp is then let down into long slate cisterns to steep before placing in the beating machine.

An arrangement for bleaching by means of chlorine gas is exhibited in Fig. 203. The gas passes from the generator, *a a*, into a wooden chamber, A, in which the damp pulp is arranged on shelves. These shelves have openings admitting the chlorine gas as shown by the arrows. The surplus gas escapes through opening, *c*, to a reservoir, which is also used for bleaching the pulp. The pulp is then removed, washed by a solution of soda, potash, or urine, and after standing, worked with antichlore, a term given by bleachers to any salt that neutralises the pernicious after effects of chlorine upon the pulp. By this means, in each 100 kilos. of half-stuff, 2·5 to 5 kilos. of common salt is developed by the action of the chlorine gas upon the soda. When bleached by chloride of lime, 1 to 2 kilos. are applied to 100 kilos. of pulp. When greater smoothness is required, a little hydrochloric or sulphuric acid is added, although care must be taken in its use, for applied too largely it destroys the fibre. Orioli employs hypochlorite of aluminium, known by the name of Wilson's bleaching preparation, chloride of aluminium being obtained on the one hand, while, on the other, all the bleaching effects arise from the delivery of ozonised oxygen ($Al_2Cl_6O_3 = 3O + Al_2Cl_6$). Varrentrapp's hypochlorite of zinc, under the name of Varrentrapp's bleaching-powder, is worthy of notice as being extensively used. In this powder, chloride of lime, decomposed with zinc vitriol, or, better, with chloride of zinc, is employed. When bleached by chloride of zinc, the mineral acid decomposes the chloride of lime, therefore no risk is incurred by the fibre.

Fig. 203.



Antichlore. When the bleach retains chlorine, it is washed in soda, potash, or antichlore, to neutralise the adhering hydrochloric acid, which merely washing in water would not effect. The chief constituents of antichlore are sulphite of soda, chloride of tin, and hyposulphite of soda. A molecule of sulphite of soda ($Na_2SO_3 + 7H_2O$) removes 1 molecule of chlorine (Cl_2), whilst hydrochloric acid and sulphate of soda are formed. A mixture of sulphite with carbonate of soda is employed to neutralise the hydrochloric acid. The sulphate of soda and chloride of sodium are removed by washing. Sulphite of calcium is greatly approved, and is considered to be as effective as antichlore, when applied as the corresponding sodium salt. A molecule of tin-salt ($SnCl_2+2H_2O$), is taken up by a molecule of chlorine (Cl_2), by which chloride of tin ($SnCl_4$) arises. After the working is completed, so much carbonate of soda is added as is required to saturate the hydrochloric acid. A molecule of hyposulphite of soda ($Na_2S_2O_3+5H_2O$), absorbs 4 molecules of chlorine, whilst sulphate of soda, hydrochloric, and sulphuric acids are formed. Some salts of lime are also commercially known as antichlore.

Blueing. Notwithstanding the careful chemical bleaching, the pulp has still a yellow tinge, and requires a colouring matter which is generally introduced in the process of beating. The blues generally used are ultramarine, Paris blue, indigo, aniline blue, oxide of cobalt. With 100 kilos. of the dry paper stuff, 0·5 to 1·5 kilos. of ultramarine are mixed, according to the strength of the colour required.

Sizing. The pulp requires sizing to preserve the colour. It is guided, as it issues from the hollander, through a tub of size, and afterwards carried over skeleton drums, containing revolving fans to dry it as it passes; heated cylinders are also used for drying. Starch is used to give a thicker consistence to the size, which is generally made from the best glue, resin being added in quantities, never exceeding 3 kilos. per 100 kilos. of pulp, to impart the desired amount of stiffness.

a. *Hand Paper.*

Straining the Paper Sheets. There are three ways of straining or filtering the pulp:—First, by straining through a brass sieve with fine slits to allow the pulp to pass, and retaining all lumps and knots. Secondly, by pressure; and thirdly, by evaporation. In the first operation the sheet is formed by a mould of the size required, being dipped into a tub of pulp previously strained. The pulp becomes distended to a thin layer and the water filters off. The tub is either round or of a quadrangular shape made of wood, lined with lead. A broad board running across the tub is called the bridge, and a smaller one under the larger one the little bridge. The large bridge has a pointed support, technically termed the donkey, for the form or frame to lean against.

The sifting machine, technically termed the knotter, used in the manufacture of hand-paper, consists of an upright cylindrical sieve, in which an inner cylinder revolves. As the whole-stuff is taken from the tub, the remainder becomes massed together, and steam or other pressure is employed to force the pulp through the sieve and cylinder, the latter retaining the lumps and knots. The paper forms, upon which the whole-stuff is placed, are constructed with brass wires to allow the water to drain off, retaining the pulp. There are two kinds of forms:—

1. The Ribbed form.—A square or oblong frame of oak or mahogany with parallel brass wires and cross wires at intervals to steady them. Lined paper is made on this form, and is not much glazed on account of the time and expense, being reckoned an inferior paper.
2. The Vellum Form.—A frame of finer brass wire-work. Vellum paper is made on this form, and has a delicate even surface; it can be made to present any degree of glossiness by pressing and satining. When held to the light it appears uniform, not possessing bright and opaque lines as in the former paper.

A ribbed form similar to the vellum form is employed in the manufacture of paper distinguished by trade marks, coats of arms, &c., the impress of the wire forming what is termed the water-mark; bank-notes are made separately in a mould in this way. The edge of the form makes the edge of the paper, forms being used according to the size required; also the quantity of the whole-stuff varies in accordance with the required thickness of the sheets. Felt is extensively used in the manufacture of paper; it is unlike the ordinary felt for hats, being a coarser, looser, white woollen fabric, more suitable for rolling.

The work of the pulp-tub is divided into two parts, the squaring and the scooping; the latter is the placing of the pulp in the mould, the former the placing of the sheets between felt. The tub is stirred occasionally with a pointed stick, technically termed the scoop stick. The pulp is taken out on the form in a sloping position, shaken a little to aid cohesion, and finally placed on the small bridge. The next sheet is placed on the large bridge. The form is laid in a sloping position against the donkey-rest to drain, and the paper finally placed on the felt to dry a little, the empty form returning to the tub. The first paper sheet is covered with felt, on which the next is placed; the average number of sheets manufactured exceeding 5000 a day.

Pressing the Paper. As soon as there is a sufficient number of sheets, they are made into a thick bale and placed under the press, the number of sheets comprising a bale being generally 181. Three bales, $181 \times 3 = 543$ sheets; twenty quires $= 480$ sheets sized, and 500 unsized. Pressing gives firmness and glossiness, and by continued pressing exceeding smoothness is obtained.

Drying the Paper. The process of pressing has not quite removed the water from the paper, which has to be dried in an airy chamber, the sheets being placed separately, or two to five together as required. An expert workman can place 800 to 900 layers of two to five sheets each in a day, as well as hanging and drying the sheets and taking them off the cord.

Sizing the Paper. The paper is not durable unless it is sized, and is only used for filtering, packing, printing, or scribbling papers. Sizing gives the paper substance by filling the pores, and making it firmer, stiffer, and harder. Ordinary size dissolved in water will not always prove effective, and it is necessary to add a solution of an aluminium salt, such as that of alum, sulphate of alumina, or chloride of aluminium, to prevent decay. Without chemical preparation the sheets are rendered sticky and have to be sized separately, but with the above addition 80 to 100 sheets can be successfully sized by hand; a good workman can size 40,000 to 50,000 sheets in twelve hours. The sheets must not be dried too quickly after sizing.

Preparing the Paper. After the sized paper is pressed and dried, it requires further preparation to make it fit for use. The first process consists in the finishing or trimming to remove all the little specks and blemishes, and to smooth the sheets. The finished sheets are counted and placed together, the workman by continued practice counting 8000 to 15,000 sheets as he places them, and separating them into whole and half quires, twenty-four sheets of sized and twenty-five sheets of unsized paper making a quire; the upper and under quire of each ream being placed on an extra sheet, known as *outsides*. The even and glazed surface is mostly obtained by hot-pressing, when every sized sheet is interposed between two unsized sheets; this is called *interchanging*. The preparation of the various kinds of paper is now accomplished, with the exception of the finest letter paper, which requires an extra process to give it a final gloss, by pressing between the rollers of the satining machine. The different varieties of paper are classed under three denominations:—

The Different Kinds of Paper. A. Writing and drawing paper, the smaller kinds of copy paper, deed paper, the finer post and letter paper, and vellum letter paper.

B. Printing paper for books, as distinguished from copy printing, deed printing, post and vellum printing, note and copper-plate printing paper. Silk papers for valentines, ornamented with gold or silver, and printed from engraved copper plates.

C. The looser textured papers, such as unsized parcel paper; the better kinds are filter- and blotting-papers. Packing paper is half-sized, and appears as a yellow straw paper, blue sugar paper, and pin and needle papers.

β. *Machine Paper.*

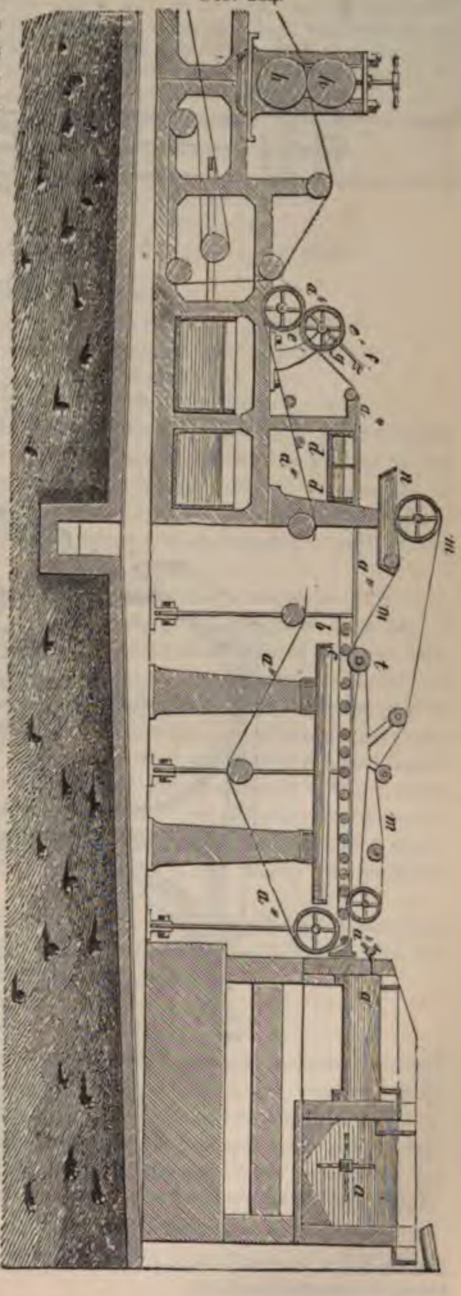
Manufacture of Machine Paper. Manufacturing paper by hand requires much time and labour, and machinery is found to be quite as efficient. Endless paper of any breadth can be made by machinery with the same amount of strength and firmness as hand paper. The straight form and the vibrating machine are used for finer paper.

1. It is requisite that the machine should make the pulp of a suitable consistence by diluting it with water.
2. Purify the whole-stuff from knots.
3. When free from knots work the material by means of regulators, delivering the stuff from the form, and producing by the uniform flow of the pulp a smooth paper leaf of the breadth required.
4. Be so regulated that the stream of whole-stuff may form a sharply turned leaf.
5. Free the paper leaf from water, so that it only requires drying in an airy chamber and pressing.
6. For removing the water, steam cylinders are principally used.
7. The finished paper is cut into sheets by the paper cutting machine.

After the whole-stuff is thinned to a consistence easily moved by water, it flows to the knotter, placed in a perforated cylinder of sheet brass, which is supplied with an interior mechanism revolving with greater velocity. One of the best knotting machines is Mannhardt and Steiner's, of Munich. After the whole-stuff is purified by the knotting machine it passes out, and the whole-stuff reservoir is supplied anew. In course of time the consistence becomes altered, sometimes producing a thicker sheet than required; this variation is obviated by the regulator, an essential in the paper manufactory. A complete paper machine is shown in Figs. 204 and 205. The drawing is divided into two parts; Fig. 205 is seen as the continuation of Fig. 204. After the whole-stuff has passed from the knotting machine, *a*, it flows into the small trough, *a′*, and is forwarded by the regulators to the form. The form, *a″ a″*, is an endless wire sieve, similar to the vellum form, the upper part extending horizontally over a number of copper rollers. The forms are from 3 to 4 metres long, and 1 to 1·6 metres broad, and are moved by means of a band passing over pulleys. Next to the regulators, *a′*, the rollers lie closer together. The form of course has a double motion, advancing in the direction of the paper sheet, which is carried to a vacant part of the wire and deposited, the form completing its circuit underneath. Periodically the form receives a shaking or vibratory movement breadthways. The paper has sometimes an uneven margin, and to equalise the substance of the layer, two fine brass wires are placed near the under edge of the form, while leather bands, *m m*, kept in place by the pulley, *t*, are placed on both sides of the form to keep the sheet straight, the bands passing through a vessel of water, *n*, to cleanse them of the adhering pulp. The water in the cistern, *c*, cleanses the wire-work forms. It is now necessary to commence the drying of the pulp; this is effected by an air-pump, or preferably by suction apparatus placed in the box, *d d*, over which the whole breadth of the paper sheet passes. After the paper leaf passes the box, it is pressed under a wirework cylinder, *e′*, under which is a corresponding cylinder; these perforated rollers are called dandy rollers. The paper sheet is now somewhat pressed and dried; the empty form returns, and the leaf passes free from the form over an endless felt to the wet press, *h h*, which consists of two iron rollers; one glazing the paper, the other passing the leaf to another pair of rollers, *h′ h′*, Fig. 205, which press and dry the leaf. The paper leaf is finally submitted to the dry press, which consists of a larger cast-iron cylinder, *u*, *v*, *w*, interiorly heated to nearly 130° C. by steam. These cylinders and the corresponding rollers, *u′*, *v′*, *w′*, are covered with felt. By the double pressing, the paper becomes dry and requires damping before the final pressing. The press *w w* is not so effective as *v v*, as it dries the surface unevenly, causing one side to be more glazed than the other. The finished paper passes under the roller, *y*, to the windlass, *j*, and is transferred by means of the arm, *k*, to the windlass, *j'*, where it arrives at its journey's end. It is then cut into sheets of the size required, by the paper-cutting machine.

Paper-Cutting Machine. When finished by the machine, the paper is cut off into long lengths and rolled by hand for the manufacturers of drawing and wall paper, scene-painters, &c. Attached to a large wheel is a knife, whose regular strokes cut the paper into the size required. The clipping machine is used for cutting the edges of books.

FIG. 204.



γ. *Pasteboard and other Paper.*

Making Pasteboard. Pasteboard is made in three ways:—

1. By placing the pulp in a form —form-board.

2. By pressing several damp sheets to form a thick card—elastic pasteboard.

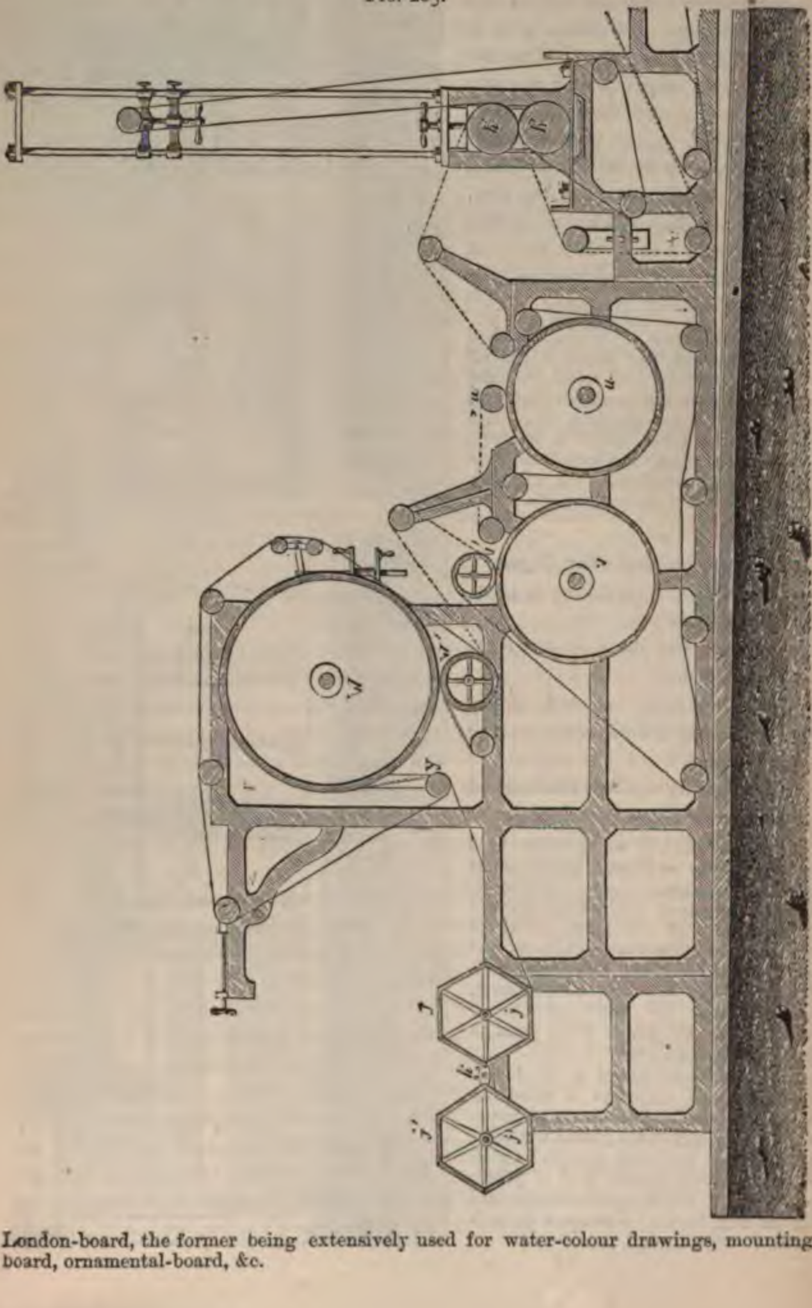
3. By pasting together the finished paper sheets—sized pasteboard.

1. Form-board is an inferior kind employed for ordinary purposes of packing, bookbinding, &c. It is made from waste paper, refuse rags, and the coarser parts of the pulp. Clay or chalk is sometimes present to 25 per cent. of the weight of this pasteboard. It is made in a coarse ribbed form, goes through the same process of knotting as the paper sheet, and is dried and pressed under a roller.

2. Elastic pasteboard is of better material, and presents a smoother surface; six to twelve sheets of paper previously damped are placed together, and pressed into one compact sheet. A separate and harder kind of pasteboard is the thick elastic board used for binding books. The inner layer is made of coarser stuff, sawdust, &c.

3. Sized pasteboard, or cardboard, is made of two to fifteen sheets of sized paper, pressed, and satined. There are varieties of this cardboard, such as Bristol-board, London-board, the former being extensively used for water-colour drawings, mounting-board, ornamental-board, &c.

Fig. 205.



Papier maché is used for fancy articles, such as the covers for albums, inkstands, blotting-books, paper-knives, &c., as well as for the cells of galvanic batteries. It is obtained from old paper made into a pulp with a solution of lime, and gum or starch, pressed into the form required, coated with linseed-oil, baked at a high temperature, and finally varnished. The pulp is sometimes mixed with clay, sand, chalk, &c., and other kinds are made of a paste of pulp and lime, and used for ornamenting wood, inlaying, &c.

Coloured Paper. The papers made from coloured rags are the brown packing paper and coarse coloured papers, such as sugar and pin paper. Coloured pin paper requires to 50 kilos. of dry pulp the several undermentioned substances:—

Yellow	2·05 0·45	kilos. ,,	Acetate of lead, Bichromate of potash;
Blue	2·05 1·05	,, ,,	Sulphate of iron, Ferrocyanide of potash;
Green	3·00 1·05	,, ,,	Blue, Yellow;
Violet	1·05	,,	Extract of logwood;
Rose	6·00	,,	Extract of Brazil wood;
Buff	3·00 3·00	,, ,,	Oil of Vitriol, Chloride of lime.

Ultramarine and aniline blue are also used in colouring the paper. In variegated papers, chemical, mineral, and vegetable colourings are used according to the required colours. Body colours are rendered fluid by a solution of gum arabic or alum in the size, which can be applied by a brush or sponge when only one side is to be coloured. Variegated and tapestry papers are an important part of the manufacture.

Parchment Paper. Parchment, although made of animal membranes, is often confounded with vegetable parchment (*phytopergamet*). The latter is made of unsized paper treated with sulphuric acid or a solution of chloride of zinc:—1 kilo. of concentrated sulphuric acid and 125 grms. of water, in which the paper is immersed so as to equally affect both sides. The length of time differs according to the quality of the paper, the thicker or firmer paper taking a longer time to saturate; soft paper will take five to ten seconds. It is then placed in a weak solution of sal-ammoniac, rinsed in water until no trace of the acid remains, and then dried. When these operations are effected mechanically, a steam machine first pulls the endless paper through a vat of sulphuric acid, then through water, sal-ammoniac, and again water, the paper passing on over cloth rollers to dry, and finally over polished rollers to press and glaze the surface.

Parchment paper, as a rule, is of one colour; when dipped into water it is rendered soft and limp. It is used for documents, deeds, records, &c., also for drawing plans, charts, bookbinding, printing, and cards.

STARCH.

Starch granules, one of the vegetable substances most extensive in nature, always appearing organically, are the foundation which, chemically treated, yield starch as commercially known. Starch is found in most organic combinations considered in chemistry and morphology, and in which cellulose is necessarily a component, being closely allied to, if not really isomeric with, this vegetable substance; its formula is $C_6H_{10}O_5$. In following its connections it becomes the starch that, by means of chemical and physical agents, in the preparation of starch gum (soluble starch-dextrine) and sugar forms one of the most important substances presented to the consideration of the technologist. It seldom appears in a large granular form, but presents itself as a white glistening powder, which upon microscopic examination seems to be made up of various rounded bodies with rings concentric to a central spot; these lines are more plainly indented and cover a greater extent in some than in others, whilst the interior of the grain appears hollowed. The granules from different plants vary in size and form; those from wheat being smaller, whilst those from tropical products are thicker and more lenticular. Payen gives the largest dimension of the granules as 0·001 millimetre; from his researches we gain also the following examples:—

Starch granules from close Potatoes	185
" " " ordinary Potatoes	140
" " " *Maranta indica*	140
" " " Beans	74
" " " Sago Palm	70
" " " Iceland Moss	67
" " " Pea	50
" " " Wheat	50
" " " Indian corn	50

Fig. 206 shows, according to Schleiden, granules of potato starch, and Fig. 207 of wheat starch. The potato has a larger granule, and sometimes gives a finer powder than wheat.

Nature of Starch. The usual starch contains in its dry state nearly 18 per cent. water, and in this state has a tendency to form itself into globules; it has been proved that exposed to a damp atmosphere it absorbs 33·5 per cent. water. Starch is insoluble in cold water, alcohol, ether, and oil. At a temperature of 160° starch yields dextrine. Starch mixed with twelve to fifteen times the quantity of warm water at a temperature of 55° varies little in substance; at a temperature of 55° to 58° it begins to change, the higher temperature making the fluid thicker. Lippmann says that potato starch is affected at 62·5°, wheat starch at 67·5°. When boiled the granules burst and form a gelatinous mass, which, largely diluted with water, can be made of a consistence to be filtered through paper, and, when allowed to cool, sets in a jelly. A stiffer paste, according to J. Weisner (1868) is made from Indian corn than from the potato or

FIG. 206.

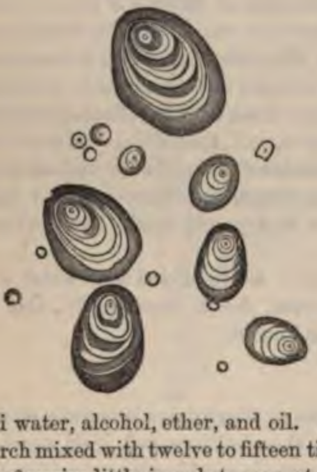
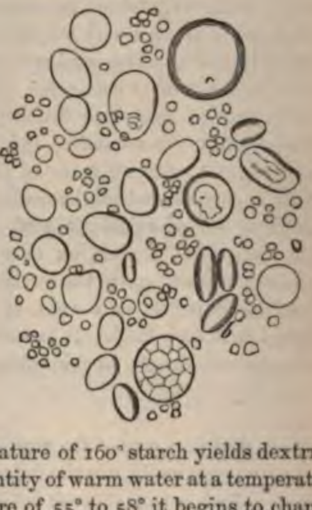


FIG. 207.



wheat. The longer the starch is boiled the stiffer the paste becomes, 1 part of starch separating in 50 parts water, and upon cooling setting into paste of a blue or violet hue. Dry starch possesses a specific weight of 1·53. Alkalies and dilute acids. with lime, tend to re-form the granules; when boiled with 2 per mille of oxalic acid, the starch loses its consistence, becoming thin, and changing into a soluble substance called *dextrine.* Starch treated with almost any dilute acid, or with diastase obtained from an infusion of malt, at the proper temperature is converted into dextrine, forming a liquid which after a few hours' standing can be made into sugar. Starch is soluble in the cold in concentrated nitric acid; water dropped into this solution precipitates the granules as an explosive combination. Under the name of *xylodine*, or white gunpowder, this combination has lately been employed for pyrotechnical experiments. By boiling starch with concentrated nitric acid, a formation of oxalic acid is obtained, evolving nitrous vapours. Starch paste upon exposure to the atmosphere becomes sour, forming lactic acid.

Sources of Starch. But few vegetables yield starch in large quantities: the potato yields 20 per cent.; wheat 55 to 65 per cent.; rice 70 to 73 per cent.; and the roots of *Jatropha Manihot* and *Maranta arundinacea*, palm pith, and the *Canna coccinea*, similar quantities. In Germany starch is prepared only from potatoes, rice, and wheat, the latter yielding a greater quantity of gum, and potato starch being thinner and not so gelatinous.

Starch from Potatoes. Potatoes form an important material in the manufacture of starch; their constitution is as follows:—

	Newly dug Potatoes.	Potatoes dried at 100°.
Water	75·1	—
Albumen	2·3	9·6
Fatty matter	0·2	0·8
Cellulose	0·4	1·7
Salts	1·0	4·1
Starch	21·0	83·8
	100·0	100·0

They contain 28 per cent. dry substance, or 23 per cent. insoluble substance, and 77 per cent. sap. The starch found in potatoes is of cellular construction; the cell walls require breaking up to fit it for manufacture. Fig. 208 shows, according to Schleiden, a fine specimen of a healthy potato under the microscope. On the outside of the potato a layer of flat, pressed, brown cells are found, sometimes appearing in a patch, *a*, forming the outer skin of the potato, and covering the cells, *b*, which sometimes contain a finer grain, but mostly a clear fluid. These cells become wider as they near the interior of the potato. The series of cells, *c*, enclose the inner cells, *d*, the pith of the potato. When the potato is dried, the cells separate from each other, as in Fig. 209, a specimen of a mealy potato. The starch granules swell in each cell, the cells uniting in reticulated streaks. The process of manufacturing starch consists in:—

1. Triturating the fresh potato.
2. Washing the starch granules from the pulp.
3. Purifying and drying the starch.

The potatoes are placed in a grinding cylinder, which formerly consisted of wood, with iron plate rollers placed half way in water to cleanse the pulverised potato pulp. Of late grinding cylinders with saw-teeth are used (Thierry's machine). The saw-blades have short teeth, lacerating the cells to obtain the starch granules, which mere gentle washing and grinding would not effect; the cylinder revolves 600 to 700 times a minute.

One cylinder with knives 0·50 metre in length and saw-blades of 0·40 metre, can grind fourteen to fifteen batches in an hour to a pulp, which is afterwards submitted to the process of washing. A cylindrical metal sieve is generally used for separating the starch granules from the potato pulp; it contains a pair of brushes slowly rotating, whilst water is supplied to the sieve to wash the pulp, which is ground to a consistence that will admit of its readily flowing off, in order that fresh pulp may be received on the sieve. The starch granules are suspended in the water strained off, and finally settle to the bottom as a soft white powder. Laine's uninterrupted cleansing sieve is now generally used; it consists of a series of wire-work frames placed over a trough. The potato pulp flows from the grinding cylinder to a space under the cleansing sieve, from thence over two gratings, where the pulp is cleansed by a stream of water playing all over it, the granules settling down at the bottom of the trough. The granules are then crushed between steel rollers to separate the starch from the fibre. 80 to 100 cwts. potatoes can be thus prepared in a day. From the above method of preparing starch from the potato we gain the general principles of such operations. The structure of the potato is shown to be partly chemical, partly mechanical, and by destroying the latter we gain starch, which is separated after the potato pulp has been standing eight days, when it becomes a white pasty mass containing starch. This is placed in a coarse sieve, which retains a greater part of the fibre, another finer hair sieve being used to receive the starch and finer fibre, separated from each other by means of a cleansing apparatus, which washes the fibre away, leaving the starch granules and sugar behind.

FIG. 208.

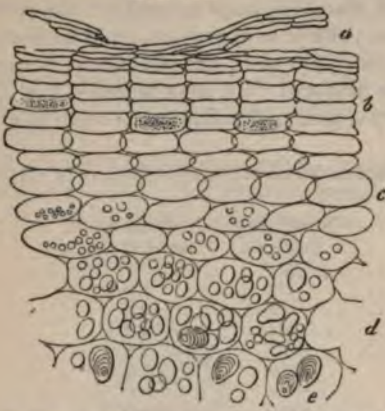


FIG. 209.

Drying the Potato Starch. The result of the washing is a milk-like fluid, which settles at the bottom of the trough as starch; it is then mixed with fresh water and allowed to solidify into a hard substance, which is cut into pieces, poured upon a linen cloth placed on a hurdle, with a plaster-of-Paris vessel, or a vessel containing gypsum, underneath, to dry the starch. After being watered and left to stand for twenty-four hours, the starch dries to the thickness of 2 decimetres upon the gypsum. Of late the water has been removed by a centrifugal machine. The moist starch contains 33 per cent. water, and is called fresh starch. The average temperature of the drying rooms is not over 60°. When the starch is dried it is broken into pieces by iron rollers. The stalk or whole starch is made by boiling to a thick paste, which is forced by machinery through a small opening into a trough, where it dries in a kind of mould.

Preparation of Wheat Starch. According to M. O. Dempwolf, 1869, the unprepared wheat contains:—

Water	10·51
Ash	1·50
Gum	14·35
Starch	65.40
Fatty and woody fibre	8·24
	100·00

From the constituent parts of wheat it is seen that:—

Starch ⎫
Gum ⎬ are insoluble in water.
Husk ⎭

Salts ⎫
Albumen ⎬ are soluble.
Dextrine ⎭

The first three are insoluble, the gum, however, being gradually dissolved by the lactic acid developed from the seed, while the starch and husk remain unattacked.

The different modes of preparing wheat starch are, namely:—

A. By fermentation (old method) of the—

α. Unground ⎫ Wheat.
β. Ground ⎭

B. New mode of treatment without fermentation.

The old method consists of the following operations:—

1. Fermenting the wheat.
2. Washing the starch from the mass.
3. Washing and cleansing the starch.
4. Drying the starch.

The whole wheat is soaked in water until soft. The seed is separated from the husk either by treading in sacks in a flat tub of water, or by being placed under rollers, and the pulp thinned with water to a milky fluid, in which a greater part of the starch and gum are found. After standing a day this fluid turns acid; a part of the gum becomes diluted by the action of the lactic and acetic acids, and is taken away and replaced by fresh water, the same process being gone through until the fermentation ceases, when the starch is washed with water and dried. In the fermentating tub it forms with the water a thin, sour pulp. The time varies according to the temperature; all the gum is not separated until about twelve to thirty days. The sour water contains acetic acid, lactic acid, butyric acid, succinic acid, ammoniacal salts, and the mineral constituents of the wheat. The mass is then placed in a sack and trodden, the milky fluid being allowed to escape, leaving the husk and refuse gum behind. The milky fluid containing starch is strained through a fine hair sieve and washed with water. Another method is that of placing the milky fluid in a tub and allowing it to settle. The first layer of the sediment is fine starch, next a mixture of starch, husk, and gum, the last layer containing but little starch. In the preparation a little ultramarine blue is added during the cleansing process. Of late the centrifugal machine has been used for the purpose of drying the starch.

Preparing wheat starch without fermenting:—

According to E. Martin's treatment, wheat flour is mixed with water to a paste, 100 parts flour to 40 parts water; the paste remains ½ to 2 hours to affect the gum, and is then washed in a fine wire sieve placed over a tub. The starch is found at the bottom of the tub mixed with water, and is placed in a warm spot to ferment slightly. It is dried in a mass, and goes through similar processes to the other starch, being made into stalk and powder starch, and sold in packets.

100 parts of wheat flour yield 25 per cent. of gum (*gluten, gluten granulé*), with 33 per cent. of water; the fresh gluten is mixed with a double weight of flour, the paste

rolled into long strips, and ground into granules, which become dry at 30° to 40°, and are afterwards sifted. The consumption of this granular gum is extensive, it being employed for food (with ordinary flour as macaroni), art purposes, and manufacture.

Constituents and Uses of Commercial Starch.

According to M. J. Wolff, the constituents of commercial starch are as follows:—

	1.	2.	3.	4.	5.	6.
Water ..	17·83	15·38	14·52	17·44	14·20	17·49
Gum ..	—	—	0·10	traces	1·84	4·96
Fibre ..	0·48	0·50	1·44	1·20	3·77	2·47
Ash ..	0·21	0·53	0·03	0·40	0·55	1·29
Starch ..	81·48	83·59	83·91	81·32	79·63	73·79
	100·00	100·00	100·00	100·00	100·00	100·00

1. The finest white patent starch in stalks, of a bright and crystalline appearance, made from pure potato starch. 2. The finest blue patent starch, potato starch coloured with ultramarine. 3. Pure wheat powder. 4. Fine wheat starch in pieces 5. Medium fine wheat starch in yellowish-white pieces. 6. Ordinary wheat starch in greyish-yellow coarse pieces, that upon microscopic examination appear as a mixture of potato and wheat starch. Starch is used for stiffening domestic articles in washing, for stiffening paper, and extensively in linen and cotton manufacture in gum, syrups, sago, vermicelli, &c. It is also a basis from which we can obtain sugar. Potato starch is preferred for domestic washing, but where great stiffness is requisite, wheat starch is used, as in bookbinding, &c. In wheat starch, the paste is formed of closely united gelatinous particles, which are more widely disseminated in potato starch, the latter being transparent and more suitable for stiffening fine linen, ironing smoother, and not sticking. Wheat starch will keep fresh upon exposure to the atmosphere longer than potato starch, the latter turning sour after a day's standing.

According to C. Wiesner, 1868, maize starch possesses the highest, wheat the next, and potato starch the most inferior stiffening qualities. Maize and wheat are considered the best for forming a smooth equal paste. Sugar can be prepared from starch by means of the active principle of malt—diastase. From this sugar, again, brandy and spirits can be distilled. According to the researches of Lüdersdorff:—

100 pounds of potato starch need 25·5 pounds of dry malt, and
100 pounds of wheat starch ,, 90·5 ,, ,,

to effect the full conversion of the starch into sugar.

Rice Starch. Chestnut Starch. Cassava Starch. Arrow-Root.

Rich starch is largely manufactured in England, France, and Belgium. To extract the gum, rice is placed in a bath of weak soda solution—287 grms. of caustic soda to the hectolitre. After standing twenty-four hours, the rice grain becomes softened, and is then washed, ground between rollers or mill-stones, and placed on a sieve with brushes to retain the husk or bran. The water strained off contains the starch, which is washed, dried, and manufactured into the form required. The gum-containing alkaline ley being neutralised with sulphuric acid is fit for inferior uses. J. and J. Colman's rice starch manufacture employs 1000 workpeople, and the result of their manipulation is used as the customary washing starch, the stiffer and brighter starch for ball dresses, window hangings, and for the size in paper manufacture.

In France the chestnut is used for the manufacture of starch. Chestnuts produce a starch possessing the evenness of potato starch with the stiffness of wheat starch. 100 parts of the fresh bitter chestnut give 19 to 20 per cent. dry starch.

Arrow-root is obtained from the *Maranta arundinacea*, and *M. indica*, cultivated in the West Indies; it is very like potato starch, and is prepared in a similar manner. Cassava starch is made from the root of *Jatropha Manihot*, or *Manihot utilissima*, and *M. Aipin*, largely cultivated in South America, the West Indies, and the Brazils.

Cassava is used as an article of consumption both in Europe and the tropics. The root of the manioc is thoroughly purified from its poisonous juice, being coarsely ground to allow the sap to escape, and roasted in an earthenware vessel, the cassava forming into granules on the sides of the vessel (*Cassava sago*, or *Manioka*), the prussic acid contained in the root becoming volatilised. From arrow-root and the analogous roots containing a poisonous juice, arrow-root derives its name, having been used by the Indians as a poison for the tips of their arrows. Its components, according to Benzon, in 100 parts, are—Volatile oil, 0·07 parts; starch, 26 parts; 89 per cent. of the starch being obtained in a powder, while the remainder is extracted from the parenchyma by boiling water; albumen, 1·58 parts; gum, 0·6 part; chloride of calcium, 0·25; insoluble fibrin, 6 parts; and water, 65·5 parts. It is known in commerce in several varieties, viz.:—Portland arrow-root, *Arum vulgare;* East India arrow-root, *Curcuma augustifolia;* Brazilian arrow-root, *Jatropha Manihot;* English arrow-root, from the starch of the potato; Tahiti arrow-root, *Tacca oceanica.*

Sago. Sago is made from the soft central portion of the stem of the palm, *Sagus Rumphii.* According to J. Weisner, the Guadeloupe sago is prepared from *Raphia farinifera*, and an East Indian variety from *Caryota urens.* The stem is torn to filaments and elutriated on a sieve with water. The starch obtained is then washed, dried, and sifted into a copper plate, where it remains a hard granular substance. A greater part of the common sago is manufactured from potato starch, coloured with oxide of iron or burnt sugar.

Dextrine Dextrine, gommeline, moist gum, starch gum, or Alsace gum, isomeric with gum arabic, and expressed by the formula, $C_6H_{10}O_5$, is formed by boiling starch with a small quantity of almost any dilute acid, which thins its consistence, and converts it into a soluble substance similar to gum arabic. It is soluble in cold water, insoluble in absolute alcohol, but slightly soluble in weak spirits of wine. Dextrine derives its name from *dexter*, the right, from the action of this substance on polarised light, twisting the plane of polarisation towards the right hand. Dextrine in grape sugar is converted into dextrose by the action of dilute acids. Dextrine solution does not ferment with yeast; but a little yeast mixed with a large quantity of gelatinous starch, at a temperature of 160°, quickly liquefies it, dextrine being produced, the greater part of which, if allowed to stand, becomes converted into grape sugar. From this decomposed dextrine a cheap and largely employed substitute for gum arabic is obtained. The components of this decomposed dextrine, according to the analyses of R. Forster (1868) are:—

	1. Dextrine.	2. Opaque Starch.	3. Dark Dextrine.	4. Gommeline.	5. Old Dextrine.	6. Bright Starch.
Dextrine	72·45	70·43	63·60	59·71	49·78	5·34
Sugar..	8·77	1·92	7·67	5·76	1·42	0·24
Insoluble substances	13·14	19·97	14·50	20·64	30·80	86·47
Water	5·64	7·68	14·23	13·89	18·00	7·95
	100·00	100·00	100·00	100·00	100·00	100·00

Potato starch is preferable to wheat starch for the manufacture of this material, not only on account of its cheapness, but for its greater purity at an equivalent price.

Dextrine is prepared by :—

a. Gently roasting.
b. Carefully treating with nitric acid.
c. Boiling with dilute sulphuric acid.
d. Treating with malt extract (diastase).

Preparing dextrine by means of gentle heat is an easy operation. The starch is roasted until it becomes brown-yellow in colour, in a large copper or iron plate cylinder, similar to a coffee drum, situated on one side of the oven. Dextrine is formed at a temperature of 225° to 260°. According to Heuzé, the following is a better method :—2 kilos. of nitric acid, of 1·4 specific weight, with 300 litres of water, are mixed with 1000 kilos. (= 20 cwts.) of starch, and boiled to form a mass, which, when exposed to the air, becomes dry. It is sometimes affected at 80°, but it becomes a paste at 100° to 110°. The starch changes into dextrine in an hour or an hour and a half at the most; it is white and soluble in water. Sulphuric, hydrochloric, and lactic acids will produce dextrine; and by the addition of water to dextrine, dextrine syrup, or gum syrup, is obtained.

Dr. Vogel gives a simple experiment to illustrate the action of dilute sulphuric acid upon starch. Nearly all kinds of writing paper are so very largely sized with starch, that if figures or letters are traced on the paper with very dilute sulphuric acid, and then dried, the application of iodine in a dilute solution will impart a blue tinge to that portion of the paper not affected by the acid, the characters remaining white.

Dextrine is extensively used instead of gum arabic in printing wall papers, for stiffening and glazing cards and paper, for lip glue, surgical purposes, wines, and in the fine arts it is applied in many ways.

SUGAR MANUFACTURE.

History of Sugar. Sugar has been known in the East Indies and China since a very remote period. In Europe honey was used for sweetening purposes in the olden time, and although sugar was known to the inhabitants of Greece and Italy, the commercial intercourse with India being limited, it was but little used until the time of Alexander the Great. After the conquest of Arabia sugar-canes were propagated in Western Asia, Africa, and Southern Europe. The Crusaders became acquainted with this useful product, and the Venetians began to cultivate it about that time in Europe and Northern Africa. Malta, Cyprus, Candia, and Egypt, yielded the first sugar-cane, which was next cultivated in Sicily, Spain, Portugal, and the Canary Islands, about 1420. In 1506, sugar was cultivated in the West Indies, Brazil, Haiti, and in many islands of the Indian Ocean. Cane sugar, a substance found in the juice of various grasses, was first discovered in South America. Ritter mentions it as a plant capable of great cultivation, to be found in different parts of the globe—eastwards from Bengal to China; westwards, the Indies, North Africa, Southern Europe to America. Slaves were imported to cultivate the sugar-canes in North America in 1800, when the first cultivation commenced, and sugar, which until now had been a curiosity and a luxury, being chiefly used for medicinal purposes, became one of the daily necessaries of life. The art of extracting sugar from the canes and refining the raw product soon became known, and this useful article of food was extensively manufactured.

Nature of Sugar. Sugar is known as cane sugar and grape sugar, dextrose, glucose crumbling sugar, starch sugar, potato sugar, and coarse raw sugar or fruit sugar

Cane sugar is prepared from the sugar-cane, maize, the *Andropogon glycichylum*, the sap of the sugar maple, the birch, the sweet turnip, and carrot. According to W. Stein, 8 per cent. of sugar is found in the root of the madder. The pumpkin, melon, banana, and most of the species of palms yield sugar. Cane sugar has the formula $C_{12}H_{22}O_{11}$. The crystallised sugar, known as sugar-candy, is hard and has a spr. gr. of 1·6; it is unaffected by exposure to the air, and when heated at a temperature of 180° it dissolves into a sticky colourless fluid, which upon rapid boiling resolves itself into a pliant uncrystallised mass, commonly known as barley-sugar. At a very high temperature it becomes black and decomposed. At 210° to 220° cane sugar becomes a dark brown substance termed *caramel*, used in colouring spirits, and for other purposes. Sugar has a pure sweet taste, is soluble in one-third of its weight of cold water; by continued boiling it loses its power of crystallising. It is insoluble in absolute alcohol and ether, but soluble in dilute alcohol, especially when warmed. Gerlach, 1864, gives in the following table the specific weight of sugar solutions with the corresponding percentage of cane sugar at 17·5° C.:—

Percentage Cane Sugar.	Specific weight Sol.	Percentage Cane Sugar.	Specific weight Sol.	Percentage Cane Sugar.	Specific weight Sol.
75	1·383342	49	1·227241	24	1·101377
74	1·376822	48	1·221771	23	1·096792
73	1·370345	47	1·216339	22	1·092240
72	1·363910	46	1·210945	21	1·087721
71	1·357518	45	1·205589	20	1·083234
70	1·351168	44	1·200269	19	1·078779
69	1·344860	43	1·194986	18	1·074356
68	1·338594	42	1·189740	17	1·069965
67	1·332370	41	1·184531	16	1·065606
66	1·326188	40	1·179358	15	1·061278
65	1·320046	39	1·174221	14	1·056982
64	1·313946	38	1·169121	13	1·052716
63	1·307887	37	1·164056	12	1·048482
62	1·301868	36	1·159026	11	1·044278
61	1·295890	35	1·154032	10	1·040104
60	1·289952	34	1·149073	9	1·035961
59	1·284054	33	1·144150	8	1·031848
58	1·278197	32	1·139261	7	1·027764
57	1·272379	31	1·134406	6	1·023710
56	1·266600	30	1·129586	5	1·019686
55	1·260861	29	1·124800	4	1·015691
54	1·255161	28	1·120048	3	1·011725
53	1·249500	27	1·115330	2	1·007788
52	1·243877	26	1·110646	1	1·003880
51	1·238293	25	1·105995	0	1·000000
50	1·232748				

A watery solution turns the rays of polarised light to the right hand. Dilute sulphuric and muriatic acids, with most of the organic and mineral acids, tend to convert cane sugar solutions into a mixture of dextrose and levulose according to the equation :—

$$\underbrace{C_{12}H_{22}O_{11}}_{\text{Cane sugar or sucrose.}} + H_2O = \underbrace{C_6H_{12}O_6}_{\text{Dextrose (glucose).}} + \underbrace{C_6H_{12}O_6}_{\text{Levulose.}}.$$

From the above it may be deduced that cane sugar is found only in the neutral juices of plants, while juices like that of the grape containing free acid, tartaric, malic, and citric acids, can yield only levulose and glucose. By treating with yeast the sugar separates and produces the usual alcoholic fermentation products, alcohol, carbonic acid, glycerine, &c. Cane sugar enters into combination with the hydroxides of calcium and barium, forming *saccharates*, which in the preparation of sugar on the large scale are of great interest. The sugar solution containing hydroxide of calcium becomes especially interesting as being the origin of the application of lime to the refining of cane and beet-root sugars, the hydroxide of calcium forming a clear fluid with a raw sugar solution containing $C_{12}H_{22}O_{11}$, becoming dull upon standing, the sediment containing $C_{12}H_{22}O_{11}.CaO$. Carbonic acid gas has of late been applied to the sugar-lime solution, the lime thrown down as carbonate and the sugar separating and becoming colourless in the solution. Preparing cane sugars with hydroxides of barium gives rise to sugar barytes, $C_{12}H_{22}O_{11}BaO$, worthy of notice as being insoluble in water and originating the method of extracting sugar from the juice of beet-root and molasses with caustic baryta. Sugar barytes is decomposed by means of carbonic acid. An explosive mixture is formed with nitric and concentrated sulphuric acids and sugar, and known as nitro-sugar. Cane sugar when mixed with a solution of sulphate of copper with an excess of caustic potash, is at first but slightly affected; a small quantity of red powder is thrown down after a time; but the liquid long retains its blue tinge, while with grape sugar the effects are much increased.

Cane Sugar.

Sugar from the Sugar-cane. The sugar-cane, *Saccharum officinarum*, is a plant of the grass species; its stalk is round, knotted, and hollow, and the exterior of a greenish-yellow or blue, with sometimes violet streaks. It grows from 2·6 to 6·6 metres high, and from 4 to 6 centimetres in thickness; the interior is cellular. The leaves grow to a length of 1·6 to 2 metres, and are ribbed. The plant is grown from seed, and also cultivated from cuttings.

A hectare of land yields raw sugar:—

	By 15 Months' Cultivation.	In 1 Year.
From Martinique	2500 kilos.	2000 kilos.
,, Guadeloupe	3000 ,,	2400 ,,
,, Mauritius	5000 ,,	4000 ,,
,, Brazil	7500 ,,	6000 ,,

Components of the Sugar-Cane. The sugar-cane yields the largest amount of sugar, generally 90 per cent. juice, containing, according to Péligot, 18 to 20 parts crystallised sugar. The components of sugar-cane, according to the analyses of Péligot, Dupuy, and Icery, are as follows:—Martinique (*a*); Guadeloupe (*b*); Mauritius (*c*).

	(*a*). Péligot.	(*b*). Dupuy.	(*c*). Icery.
Sugar	18·0	17·8	20·0
Water	72·1	72·0	69·0
Cellulose	9·9	9·8	10·0
Salts	—	0·4	0·7—1·2

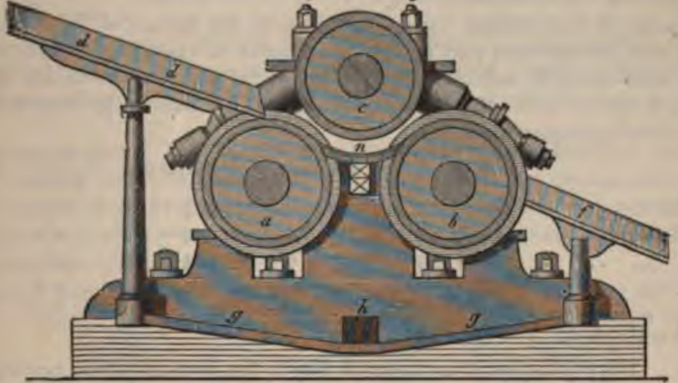
From 18 per cent. sugar found in the sugar-cane, as a rule not more than 8 per cent crystallised sugar can be realised. The loss may be accounted for thus:—90 per cent. juice is expressed from the cane, from which only about 50 to 60 per cent. can be clarified from the straw, &c.; a fifth part is exhausted by refining; and finally two-thirds of the sugar is obtained by boiling, while the rest goes to the molasses. The 18 per cent. sugar may be realised in the following manner:—

In the refuse sometimes remains	6	per cent.
By skimming	2·5	"
In the molasses	3	"
As raw sugar	6·5	"
	18	"

Preparing the Raw Sugar from the Sugar-Cane. The preparation of raw sugar from the sugar-cane consists in first expressing and then cleansing and boiling the juice.

1. *Expressing the Juice.*—The sugar-canes are crushed in a press consisting of three hollow cast-iron rollers, *a b c*, Fig. 210, placed horizontally in a cast-iron frame. By means of the screws, *i i*, the approximate distance of the rollers is adjusted. One roller is half as large as the others, and is moved by three cogged wheels fitted on to the axis of the rollers. The sugar-canes are transferred from the slate gutter, *d d*, to the rollers, *a c*, which press them a little, and from thence they are carried over the arched plate, *n*, to the rollers, *c b*. The pressed sugar-canes fall over the gutter, *f*, the expressed juice collecting in *g g*, and running off through *h*. The middle roller is termed the king roller; the side cylinders are individually the side roller and macasse.

FIG. 210.



2. *Refining and Boiling the Juice.*—The expressed juice is removed to the boiling-house, which is fitted with five iron or copper vessels. To 15,000 litres of expressed juice 5 to 9 litres of milk of lime are added. The lime neutralises the malic and other vegetable acids, and upon boiling forms with the albumen and the other constituents of the juice a thick green scum, which being removed the juice is allowed to remain in two of the pans to evaporate. A fresh scum is formed on the first pan, which returns after a second or third time of removal. The juice as it issues from the press is received into the first pan, in which by slow boiling it becomes a thick froth, changing by rapid boiling to a clear colourless fluid; in the third and fourth pans the liquid becomes gradually purer, until in the fifth it crystallises. The finger is dipped into the boiled juice to test its consistence, and by the length of the pendant drop, which ought to be about 3 centimetres, the thickness is ascertained. The boiled juice is placed in a large open wooden vessel of about 16 centimetres capacity, and termed the cooler, where after standing twenty-four hours the sugar crystallises, the cooler being provided with a double per-

forated bottom to allow the molasses to escape, leaving the crystals behind. After standing five or six weeks, the molasses dries into a mass commonly known as moist, raw, or Muscovado sugar. The molasses passes into a cistern placed underneath the cooler, capable of containing 15,000 to 20,000 litres of juice, and after standing fourteen days is ready for the market. In the French and English colonies sugar is exported in chests covered with fire-clay under the name of chest or tub sugar.

Varieties of Sugar. European commerce deals with the following kinds of raw sugar :—

1. West Indian—Cuba, San Domingo or Haiti, Jamaica, Porto-Rico, Martinique, Guadeloupe, Saint Croix, St. Thomas, Havana.

2. American—Rio Janeiro, Bahia, Surinam, Pernambuco.

3. East Indian—Java, Manilla, Bengal, Mauritius, Bourbon, Cochin China, Siam, Canton.

Of late there has been a distinction between sugar cultivated by slave and that by free labour; the latter comes from Jamaica, Barbadoes, Demerara, Antigua, Trinidad, Dominica; the former from Cuba, Havana, Brazil, St. Croix, and Porto Rico.

The mode of manufacture varies according to the nature of the foreign substances that always form part of the constituents of sugar, such as water, fibre, gluten, sand or earth, soluble mineral salts, acetic and other acids, all of which must be destroyed before the sugar can be refined. According to Renner we have in the following sugars from :—

	Java.	Havana.	Surinam.	In Sugar-Candy.	In Balm.
Raw Sugar	98·6—83·1	97·0—87·3	92·3—85·4	99·6	99·7
Slime Sugar	5·5— 0·3	3·7— 0·9	4·4— 1·6	0·1	0·2
Water	6·1— 0·3	3·5— 0·9	6·3— 3·6	0·2	0·1
Ash	2·1— 0·2	1·4— 0·0	2·0— 1·2	0·1	—
Caramel, gum, vegetable acids, &c.	3·5— 0·5	4·5— 0·4	2·1— 1·1	—	—

Molasses. The production of molasses is due to the long-continued heating of the cane juice, but the quality varies according to the nature and culture of the sugar-canes, the heat of the season, &c. By chemical treatment molasses appears as a concentrated watery solution of crystallised sugar, slime sugar, with a small admixture of caramel and mineral salts. It is a dull red-brown sweet fluid used principally in the colonies for the manufacture of rum; it is soon converted to spirit, and then quickly becomes acetated. Renner gives the constituents of molasses as :

Raw Sugar	32·97	40·36
Slime sugar	4·30	7·38
Water	13·71	16·25
Ash	3·35	3·78
Caramel, gum, &c.	45·65	32·22

Refining the Sugar. Sugar refining consists in :—

1. Dissolving and refining. The raw sugar is dissolved in water, and during the process cf evaporation the apparatus is connected by a gutter to a reservoir, into which the sugar flows. It is then submitted to a straining apparatus, which retains the several impurities. The refined fluid is then heated in a copper pan, termed the melting-pan, the water adding 30 per cent. to the weight of the sugar, and is afterwards placed in the refining pan, a vessel constructed with a double bottom. For the purpose of clearing, a mixture of albumen is added in the shape of serum of blood, or white of egg, with lime-water and sulphuric acid, an addition afterwards being made of 3 to 4 per cent. animal charcoal and ½ to 2 per cent.

blood, and the whole heated to the boiling-point. The albumen coagulates and forms a fibrous scum, containing all the impurities.

2. Taylor's filtering apparatus is now much used for filtering the sugar, charcoal being employed as the purifying agent.

3. The boiling of the clear sugar in pans placed over a vacuum apparatus, resembles the previous boiling, with the exception that the fluid is rendered purer, 10 to 12 per cent. water remaining.

4. Cooling and crystallising. When the sugar begins to crystallise on the surface of the vaccum pan, generally at 80°, the temperature is lowered to about 50°, as too great heat at this stage of the process exercises an injurious effect upon the sugar, which now forms an amorphous mass, and is drained, washed with clean syrup, and prepared for ordinary loaf-sugar. Sugar-candy is the result of slow crystallisation, the crystals by this means acquiring a larger size and more regular form.

5. The shaping of the crystallised mass into the form of a sugar-loaf is accomplished by evaporating the sugar and placing it in earthen conical moulds to solidify at a temperature of 25° to 30°. After standing ten minutes the sugar sets into form.

6. Drying the sugar. After standing twelve hours a green-coloured syrup is obtained from the crystalline mass, which is removed, and the crystals submitted to a centrifugal process of drying, then placed in a drying-stove at a temperature of 25°, which is gradually increased to 50°. By thus refining the raw sugar, the ordinary loaf sugar is obtained.

Production of Raw Sugar. The estimated production of raw sugar in 1870 was 55,000,000 cwts., the largest instalment being from Cuba.

Beet-Root Sugar.

Its Nature. In the year 1747 Marggraf, a chemist of one of the Berlin academies, discovered crystals of sugar in the red beet, *Beta cicla*, which he deemed capable of manufacturing into the commercial article. He found that, treated with alcohol, the white beet yielded 6·2, and the red variety 4·6 per cent. of sugar. But the preparation of beet-root sugar was not developed until the close of the year 1800. Achard and Hermbstädt, of Berlin, tried many experiments with this new product with equal success, always finding that beet-root contained crystallised sugar to the amount of 6 per cent., with 4 per cent. of molasses, and sometimes a larger quantity of sugar. About the time of the Continental war native products were in request on account of the difficulty and expense of obtaining foreign articles. The first Napoleon supported the new product in the pursuance of his "Continental system" of excluding cane sugar from the French markets, and a trial of the German method was made, but it was not crowned with the success it has now achieved until ten years after his overthrow. The annual production of sugar in 1811 did not exceed 13,000,000 lbs.; the present yearly consumption of beet-root sugar exceeds 15,000,000,000 lbs., this enormous amount being supplied by more than eighty manufacturers.

Species of Beet. The vegetable known as beet-root is a large fleshy root of the beet, a plant of the species *Beta maritima*, largely cultivated in France, Belgium, and Portugal for the production of sugar. There are several varieties of the two species, the white beet being preferred on account of its yielding more sugar, and also for its purity of colour, the red beet being chiefly cultivated for culinary purposes. There is also the field beet, commonly known as the *mangold wurzel*, which was first used as provender for cattle about the end of the last century. The sugar beet has, in course of cultivation, been improved by many new methods of manuring, &c., until it yields 13 and sometimes 14 per cent. of sugar. In Germany the following varieties of beets are principally cultivated :—

1. Quendlinburg beet, a slender rose-coloured root, and very sweet; it is matured fourteen days before any other kind. 2. Silesian beet is pear-shaped, with bright green ribbed leaves; it is known as the green-ribbed beet, and does not produce so much sugar as the former. 3. Siberian beet is pear-shaped, with white-green ribbed leaves, and is known as the white-ribbed beet. It does not yield so well as the Silesian beet, although of a greater weight. 4. The French, or Belgian beet, has small leaves and a slender and spiral root, yielding sugar. 5. The Imperial beet is slender and pear-shaped, yielding much sugar. The king beet is a biennial; in the first year the root is merely developed, in the second it bears seed.

The following is a list of the countries where the beet is cultivated for sugar :—

In	According to—	Beets gathered in cwts.	The manufacture of suitable Beets in cwts.	Into Sugar in pounds.
Austria	Krause	104—145	88—123	770—1084
Austria	Burger	169—193	143—164	1256—1560
Bohemia	Neumann	112—145	95—123	836—1160
Prussia	Lüdersdorff	146	124	1088
Prussia	Thaer	180	153	1336
Baden	Stölzel	120—160	102—136	896—1196
France :—				
Northern Departments	Dumas	193	168	1476
Other "		124	105	924
France	Boussingault	149	127	1116

In general 140 to 160 cwts. are cultivated, cut, and cleaned, per acre, there being four Magdeburg acres to one hectare, which usually yields sufficient roots for three days' work.

Chemical Constituents of the Beet.

The flesh of the beet consists of a quantity of small cells containing a clear, colourless fluid. The constituents of the sugar-beet, according to chemical analyses, are :—

Water	82·7
Sugar	11·3
Cellulose	0·8
Albumen, caseine, and other bodies	1·5
Fatty matter	0·1
Organic substances, citric acid, pectin and pectic acid, asparagin, aspartic acid, and betain, a substance having, according to M. Scheibler, the formula $C_{15}H_{33}N_3O_6$ ..	3·7
Organic salts, oxalate and pectate of calcium, oxalate and pectate of potash and sodium	
Inorganic salts, nitrate and sulphate of potash, phosphate of lime and magnesia	

Near Magdeburg, where the beet is extensively cultivated, the general results give :—

The greatest sugar production, as 13·3 per cent.
That from inferior beets, as .. 9·2 "
The average beet yielding .. .. 11·2 "

The components of the beet vary according to the time of the year, it at some periods containing more water than at others, from 82 to 84 per cent. being the average. In the autumn it does not contain slime sugar; in February and March the components intermingle and some decrease nearly 2 per cent., as shown by the following analyses:—

	October.	February.
Woody fibre and pectin ..	3·49 per cent.	2·52 per cent.
Water	82·06 ,,	84·36 ,,
Sugar	12·40 ,,	10·60 ,,
Slime sugar	0·00 ,,	0·65 ,,
Mineral salts	0·75 ,,	0·63 ,,
Organic acid and extractives	1·30 ,,	1·24 ,,
	100·00	100·00

12¼ cwts. of beet yield on an average 1 cwt. of raw sugar.

Saccharimetry. The measure of the amount of saccharine matter contained in the various crude sugar productions can be estimated either by the—

1. Mechanical,
2. Chemical, or
3. Physical method.

Mechanical Method. The middle part of the beet is cut in thin slices to the weight of 25 to 30 grms. each, and dried. From the difference in weight before and after drying, the quantity of water contained in the root is ascertained. The dry residue is pulverised, and then treated with boiling dilute alcohol of a specific gravity of 0·83. By this means the sugar is dissolved, and the weight ascertained. The insoluble residue gives after drying the weight of the cellulose, protein bodies, and mineral constituents. If the alcoholic solution be placed in a vacuum over caustic lime, it gradually becomes more and more concentrated, until after standing about a day, the sugar, owing to its insolubility in absolute alcohol, may be collected in small colourless crystals, only absolute alcohol remaining. Good sugar beets give 20 per cent. dry residue, the water amounting to 80 per cent. Of the 20 per cent., 13 per cent. is usually sugar, and the remaining 7 per cent. pectin, cellulose, protein, and mineral substances. The higher the specific weight of the juice of the beet, the more sugar it contains. The juice of a good beet properly cultivated marks 8° and sometimes 9° B.

Chemical Method. The chemical method is based upon the following facts:—

a. The known proportional solubility of hydrate of lime in cane sugar.

b. The capability of a cane sugar solution to reduce the hydroxides of copper to protoxides, the quantity reduced affording an estimate; and the conversion by acids of cane sugar into inverted sugar (a mixture of levulose with dextrose or glucose).

c. The fermentation of sugar, giving rise to the formation of alcohol and carbonic acid, the amount of which can be ascertained, $4CO_2$ corresponding to 1 mol. of cane sugar, $C_{12}H_{22}O_{11}$.

The first of these methods is that of determining the solubility of hydrate of lime in a cane sugar solution. The fluid containing sugar is stirred with hydrate of lime, the quantity of which dissolved, estimated by titration with sulphuric acid, determines the quantity of sugar. The second method is grounded on the researches of M. Trommer, who found—(1.) That cane sugar in an alkaline fluid does not reduce oxide of copper; but it becomes reduced if the sugar has previously been boiled with sulphuric or hydrochloric acid, the acid converting the cane into inverted sugar. 2. The quantity of the reduced protoxide is proportional to the quantity of sugar. Barreswil and Fehling give a test based on this law:—An alkaline solution of oxide of copper is made by dissolving 40 grms. of sulphate of copper in 160 grms. of water, and adding a solution of 160 grms. of neutral tartrate of potash in a little water, with 600 to 700 grms. of caustic soda ley of a specific gravity = 1·12. The mixture should be next diluted to 1154·4 c.c. at 15°. A litre of this copper solution contains 34·65 grms. of sulphate of copper, and requires for its reduction 5 grms. of dextrose or levulose; or 10 atoms sulphate of copper (1247·5) are reduced, by means of 1 atom of dextrose or levulose (180), to protoxide (34·65 : 5 = 1274·5 : 180, or = 6·93 : 1), 10 c.c. of the copper solution corresponding also to 0·050 grms. of dry dextrose or levulose. Mulder prefers a solution in which 1 part of oxide of copper corresponds to 0·552 part of dextrose or levulose of the formula $C_6H_{12}O_6+H_2O$; by the use of this test-liquor, the amount of sugar may be ascertained with great accuracy. By another method 10 c.c. of this copper solution are heated with 40 c.c. of water, and placed in a sugar solution till all the oxide of copper is reduced. When this point is nearly reached, the precipitate becomes redder, and forms more rapidly. Testing the filtrate with ferrocyanide of potassium will throw down a yellow precipitate if there be sugar in excess. The copper salts are instantaneously reduced by the sugar in corresponding quantities; long boiling is not necessary. 100 parts dextrose or levulose correspond to 95 parts cane sugar.

Ferment Test. The third method, the ferment test as it is generally termed, is grounded on the fact that a solution of sugar may be preserved for an indefinite period in an open or close vessel; but that if decomposing azotized matter be accidentally or intentionally added, the sugar is converted first into dextrose or levulose, which suffering vinous fermentation is converted into alcohol with the evolution of carbonic acid.

$$\left.\begin{array}{l}\text{1 mol. of cane sugar,}\\ \quad CHO=342,\end{array}\right\}\begin{array}{c}\text{yields by}\\ \text{fermentation}\end{array}\left\{\begin{array}{l}\text{4 mols. of carbonic acid} = 176,\\ \text{4 mols. of alcohol} = 188.\end{array}\right.$$

The estimation of the quantity of carbonic acid is easily performed by means of the alkalimetric apparatus of Fresenius and Will. The fermentation being complete, the air is sucked out of the apparatus, and the amount of carbonic acid estimated from its loss, which

Multiplied by $\frac{171}{88} = 1·9432$, gives the quantity of cane sugar.
,, $\frac{180}{88} = 2·04545$, gives the quantity of dextrose.

Physical Method. The raw sugar containing dextrose or dextrine rotates the plane of polarised light to the right hand in proportion to the quantity present. A sugar solution of 100 c.c. containing 15 grms. of sugar turns the ray of polarised light of 200 millimetres length, 20° to the right. Proportionally a solution of 100 c.c. containing 30 grms. of sugar, turns the ray 40°. The forms of polarimeters are very various, and this method of estimation has received attention from many eminent physicists.

Preparation of Sugar from the Beet. The preparation of sugar from the beet consists in the following operations:—

1. Washing and cleansing the beet.
2. Obtaining the juice from the root.
    - α. The root is ground to a pulp and subjected to hydraulic pressure.
    - β. The juice is extracted from the pulp by means of a centrifugal machine.
    - γ. According to Schützenbach, after the maceration juice is separated from the pulp by water.
    - δ. The root is cut into thin slices and placed in a vessel (diffusion apparatus) with water at a certain temperature.

3. Refining the juice with lime, and removing the lime with carbonic acid.
4. Filtering the juice through charcoal.
5. Boiling the refined juice for crystallisation.
6. The manufacture of raw and refined sugar.
   - α. Raw or moist sugar.
   - β. Refined or loaf sugar.

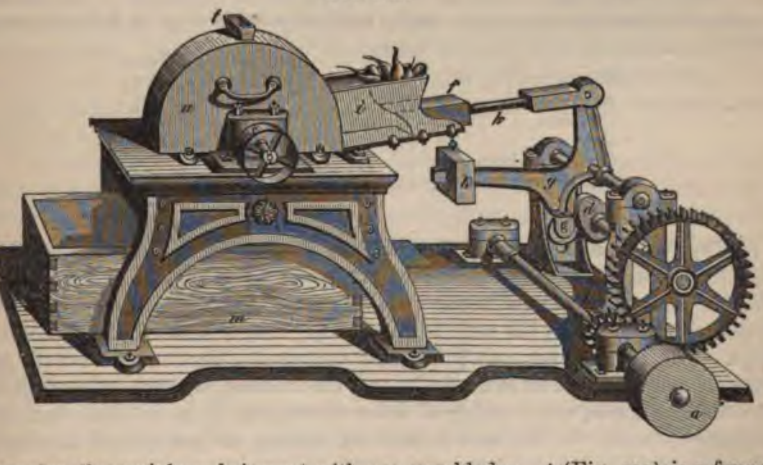
1. *Washing and Cleansing the Beet.*—The beet when newly dug requires washing and cleansing, which takes 10 and sometimes 20 per cent. from the weight of the root. Champonnois's washing machine, is, perhaps, the most successful; it consists of revolving drums of open iron- or wood-work placed in a trough supplied with water, the drums making from 8 to 40 revolutions in a minute. The beets cleansed from all impurities, washed, are cut and submitted to elutriation on a sieve. From 1000 to 1200 cwts. beets can be prepared per day of twenty-hour hours with 2-horse power; the length of the washing drum being from 3·1 to 4 metres with a diameter of 1 metre, the drum making from 30 to 40 revolutions per minute.

2. *Separating the Juice from the Root.*—There are two methods of effecting this; the first by grinding the root to a pulp, and then removing the juice by:—

α. Pressing.
β. Centrifugal force.
γ. Maceration.

The sugar in the beet-root is contained in the cells, which are easily opened, but require a moderate pressure to extract the juice containing the sugar. A hand-grinding machine is sometimes found sufficient for this purpose, but Thierry's crushing machine, shown in the following illustration, Fig. 211, is generally used. The grinding cylinder, Fig. 212, is 0·5 to 0·6 metre in length, and 0·8 to 1·0 metre in diameter, the periphery being set with 250 saw-blades. *t* (Fig. 211) is a funnel to admit water; *i* the trough into which the roots are placed; *m* the cistern to receive the pulp. The motive power gears with *a* and *s*; and the motion of the axis of *a* is by means of the pinion, *b*, communicated to the eccentric, *d*, and friction roller, *e*, thence by the arm, *g*, and connecting-rod, *h*, to the plunger, *f*, which presses

FIG. 211.



the roots against the edges of the saw-blades concealed by the case, *u*, the pressure being regulated by the weight, *k*. The cylinder revolves 1000 to 1200 times a minute, reducing from 800 to 1000 cwts. of beets to pulp in twenty-four hours. The water from *t* is necessary, that the pulp may be ground to a finer consistence.

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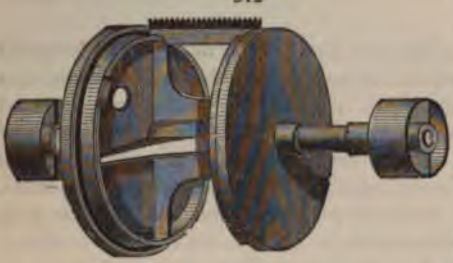


a. The juice is obtained by pressing the pulp by means of a stone or iron roller through a series of linen cloths. But in the French manufactories the hydraulic or Bramah press is most generally adopted. The pulp is placed in sacks or bags between iron plates, and subjected to a pressure of 500 to 600 lbs. Tne expressed juice flows from the bed-plate into a pipe, which conducts it to a receptacle. 100 cwts. of beet, with a pressed residue of 18 per cent., yield 82 per cent. good juice.

The Residue. According to the researches of M. Wolff, the residue of the crushers used at Hohenheim contains—

When the beets are pressed with :—

	Fresh Roots.	20 per cent. Water.	14 per cent. Water.	Without Water.
Water	81·56	68·01	67·92	65·94
Ash	0·89	5·47	5·74	5·28
Cellulose	1·33	6·25	6·04	6·68
Sugar	11·88	7·86	7·58	6·72
Protein substances	0·87	1·05	1.67	11·02
Other nutritious „	3·47	11·36	10·05	14·31

100 parts of beet leave 23·2 parts residue and 76·8 parts juice of the following composition :—

	Residue.	Juice.
Water	15·61	65·95
Ash	1·27	(?)
Cellulose	1·47	—
Sugar	1·72	10·17
Carbon hydrate	2·84	0·63
Protein substances	0·28	0·58
	23·20	76·80

β. The juice is now generally obtained from the pulp by means of the centrifugal machine to the extent of 50 to 60 per cent., water being applied to the residue to obtain a thin pulp also used in sugar manufacture. A centrifugal machine 1 metre in diameter will express 100 cwts. per day. The power to which the first juice is due is 5·1 atmospheres, 60 per cent. juice being expressed. The remainder of the juice, after the addition of water to the contents of the machine, is expressed at a pressure of 1·8 atmospheres, the quantity of water amounting to 50 to 60 per cent. of the quantity of beets. Of the roots 50 per cent. remain, 20 per cent. in the residue, and 30 per cent. in the clarifying vessel.

γ. Treating the beet-pulp according to Schützenbach's method of immersion and maceration in order to obtain the juice. The roots are cleaned and then cut in slices by a cutting machine. They are then passed to a drying chamber heated to 50°, and subsequently ground to a meal. Four parts of this meal are allowed to macerate in 9 parts water, to which sometimes sulphuric acid is added. Another method is to moisten the dried beet-meal with milk of lime, and afterwards continue the operation in a bath of water heated to 80°. These methods are largely used in Germany, where in general practice it is found that 4·75 cwts. of green roots yield 1 cwt. of dry beet-meal. The juice is afterwards treated with lime-water for the purposes of purification.

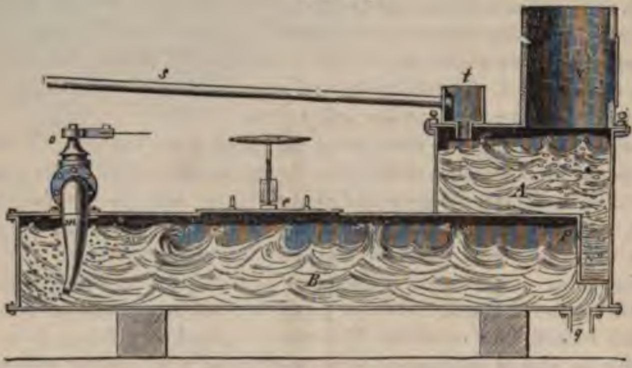
δ. Before any juice can be obtained it is necessary to open the cells in which it is confined. This, as it has been seen, may be effected by pressure or by maceration in water, by which the cells are broken and to which they yield their sugar. The action with each cell is very similar to that of the dialyser used in dialysis; the sugar becomes gradually diffused in the water, the insoluble substances remaining with the cell. By this means a very pure sugar solution may be obtained and afterwards concentrated. The diffusion residues are always very watery, containing 93 per cent. water and 7 per cent. dry substances.

Components of the Juice. The juice after being expressed from the pulp, if allowed to remain exposed to the action of the air, throws down a dark flaky precipitate. The more free acids the juice contains the lighter will be the colour of the precipitate, and the juice will appear of a brown-red. The juice is not only a solution of sugar, but contains the soluble constituents of the beet, in which nitrogenous and mineral substances are very prominent. Sugar under fermentation forms lactic acid and other products; but is is separated from all impurities and refined into crystals. The usual method of refining is to boil the juice rapidly in copper refining-vessels constructed with double bottoms. The rapid boiling separates the coagulated juice, whilst the free acid is neutralised by the introduction of dilute milk of lime. The lime also serves to separate the nitrogenous substances of the juice, and enters into a combination with a small portion of the sugar, forming sugar-lime or calcium saccharate. Lime, too, throws down from their salts protoxide of iron and magnesia, while potash and soda are set free. The quantity of lime added depends upon the condition of the root. As a rule, to 100 pounds of juice, 1 to 2 pounds of lime are added, or to 2 cwts. of roots 1 pound of lime. The insoluble combinations of lime are separated from the juice as a slime by filtering in a filtering press.

3. *De-Liming, or Saturating the Juice with Carbonic Acid.*—The clear juice is by no means a pure sugar solution, but contains besides free sugar, sugar-lime, free potash, and soda, sometimes ammonia, and a small quantity of nitrogenous organic substances. decomposed by the free alkalies, ammonia being largely developed by their evaporation. The juice also contains various organic acids (as aspartic acid) and alkaline salts (as sulphate and nitrate of potash). The decomposition of the sugar-lime effects the removal of the extraneous substances from the juice. The physical method of purifying the juice is by filtering it through animal charcoal, while the chemical method is effected by means of carbonic acid. The use of carbonic acid was first recommended by Barruel, of Paris, in 1811, and later by Kuhlmann, Schatten, and Michaelis. The latter obtained the gas from the action of sulphuric acid upon chalk, or better upon magnesite; the former employed the gas resulting from the combustion of charcoal or coke. Lately, Ozouf has prepared carbonic acid gas by heating bicarbonate of soda. In the German manufactories the decomposition of the sugar-lime is effected in a Kleeberger's pan, Fig. 213. This apparatus consists of a cast-iron cistern, B, to contain the juice. The carbonic acid, having been washed in

pure water, is admitted by the pipe, *m*, which dips nearly to the bottom of the vessel, B, and is divided internally by a partition for the better dissemination of the gas. The unabsorbed gas collects in B over the juice, whence it passes through the opening, *p*, into the upper chamber, A. When the juice sinks through *p* into B, the gas there collected passes through A into *n*, and is thence re-conducted to the reservoir. When the juice is sufficiently cleared, the carbonic acid cock, *o*, is turned off, and the juice allowed to flow into a reservoir through *q*, where the carbonate of lime settles. The clear juice is then fit for crystallisation. The man-hole, *e*, is provided for the cleansing of the apparatus from separated carbonate of lime. The juice to be de-limed is supplied to the cistern, B, by means of the pipe, *s*, and the gutter, *t*.

FIG. 213.



Other Methods of De-Liming the Juice. Instead of employing carbonic acid or animal charcoal, the lime of the sugar-lime may be removed by the addition of a substance or an acid which forms with it an insoluble body, but does not affect the sugar. Oxalic acid is suitable for this purpose, oxalate of lime being insoluble in the sugar solution, but the acid is very expensive, and, besides, the precipitate is too fine, passing through the filter. Phosphoric acid is used for the purpose, phosphate of lime separating into flakes which can be easily removed by filtering through a thin layer of charcoal. Any free phosphoric acid is converted into phosphate of ammonia, neutralising the alkali, while the excess of ammonia is volatilised on the application of heat to the juice. Oleic, stearic, and hydrated silicic acids, and casein, similarly throw down precipitates. Acar uses pectic acid, which forms with the lime an insoluble pectate. Morgenstern has found sulphate of magnesia prepared from the Stassfurt kieserite successful in removing part of the impurities as well as a portion of the colouring matter. Frickenhaus tried hydrofluoric acid. In 1811 Proust recommended sulphite of lime; and in 1829 Dubrunfaut took out a patent for the employment of sulphurous acid. Melsens, of Brussels, in 1849, employed hyposulphurous acid, which at 100° separates the lime and most of the protein substances, and disguises for a time the colouring matter, the colour, however, returning on exposure to air, and remaining permanent.

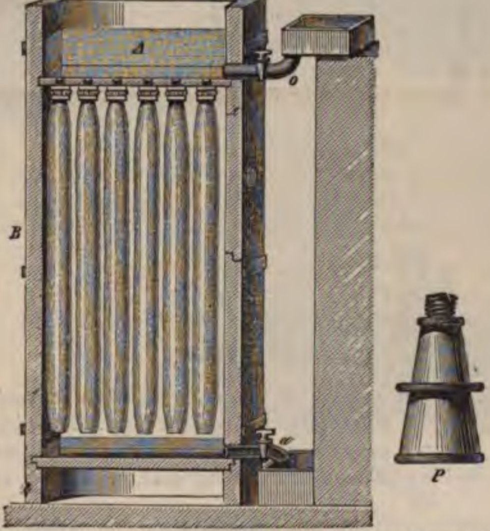
Purifying with Baryta. About fifteen years ago Dubrunfaut and De Massy patented a method of purifying the juice by means of caustic baryta, which forms with cane sugar at the boiling-point the insoluble saccharate, $C_{12}H_{22}O_{11}.BaO$; in practice sufficient caustic baryta is added to throw down all the sugar. The sugar-baryta is thus separated from the supernatant fluid in which all the foreign substances remain suspended; and is next treated with carbonic acid to form carbonate of baryta and set the sugar free. The solution is then filtered and some gypsum added, which gives rise to the double decomposition of the carbonate of baryta into sulphate, and of the gypsum into carbonate of lime.

4. *The Filtration of the Juice through Animal Charcoal, and the Evaporation of the Juice.*—The various apparatus here play the most important part.

The Filter. Besides acting as a filter, charcoal possesses the property of removing the colour from the liquid allowed to percolate through it. Wood charcoal was first used for the purposes of sugar-refining in 1798, but lately has given place to the employment of animal charcoal (bone charcoal), which, according to Schatten, has a tendency to remove the lime and salts in the juice. At first it was used in powder, but now it is employed in the form of lumps. The old method consisted in boiling the powdered charcoal with the juice, blood being afterwards added, as in the usual methods of sugar-refining.

Fig. 214 exhibits a section of Taylor's filter, which has been in use since 1825. The juice is admitted to the upper cistern, A, by means of the pipe, *o*, and gradually percolates through the long linen bags suspended from the bottom of A in B, and containing charcoal, a layer of charcoal being also placed in A. The mouth of each bag is kept open by a funnel-piece shown at P. The filtered juice is received into the lower cistern, whence it passes by the pipe, *a*, into the reservoir.

Fig. 214.



Dumont's Filter. Pajot des Charmes employed animal charcoal in 1822, but Dumont was perhaps the first to make its use successful by means of a filter still bearing his name, shown in vertical section in Fig. 215, and in plan in Fig. 216. The juice is supplied to the filter, A, from the cistern, D, the supply being regulated by the ball-cock, *d e*. The pieces of charcoal in A rest upon the sieve, *b b*, the percolating juice being received into the cistern, and removed by the tap, *o*. C is a man-hole for the cleansing of the apparatus.

Evaporation Pans. The pans generally in use for evaporating the juice to crystallisation are made sufficiently strong to withstand high steam and atmospheric pressure. The processes of evaporation are :—

I. Under the usual air-pressure :
  - *a.* In pans suspended over an open fire ;
  - *b.* With high steam pressure ;
  - *c.* By hot air.

II. By diminished air-pressure or vacuum pans, the vacuum being produced:
- *a*. By the air-pump;
- *b*. On the principle of the Torricelli vacuum;
- *c*. By means of steam and condensation;
- *d*. By combining the methods *a* and *b*.

The pans are constructed to prevent the boiling over of the juice. One of the ill effects of an open fire is the danger of over-heating, or burning as it is called, which deteriorates the quality of the sugar solution in various ways, forming caramel. Fig. 217 is a vertical section, and Fig. 218 the plan of an open pan arrangement. D is the evaporating pan, A the fire-place, C the ash-pit, E and G the flue. The fuel is placed on the sloping grid, *b*, through the furnace-door, *a*.

Fig. 215.

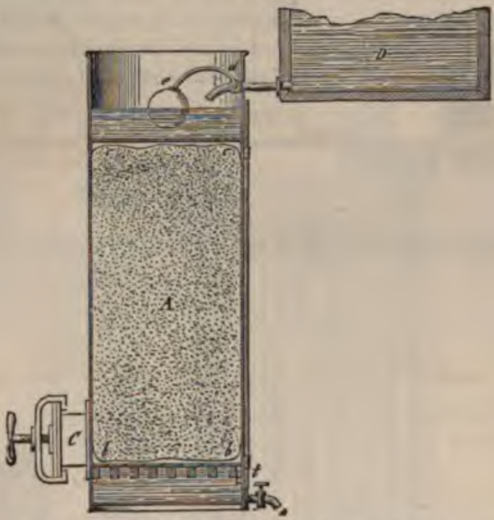
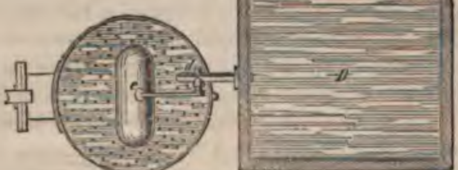


Fig. 216



The fire-room is arched, the flame and hot gases passing through the openings, *e e*, into contact with the evaporating pan; *l l* admit air to the fire-place. The use of a suspended pan, as shown in Fig. 219, is preferable for many reasons. When the juice is sufficiently concentrated, the workman has only to pull the rope, *m*, to empty the pan.

The Pecquer evaporating-pan is heated by steam, the pipes, Figs. 220 and 221, being placed horizontally under the pan. The steam enters by *a* into *b*, passes through the pipes, and is conveyed away by *d* and *e*. The heating by steam.

besides the advantage of cleanliness, is more equable and easily managed. When the juice is sufficiently heated, the pan, by means of the lever, *m*, is tilted up, and the juice run off by opening *g*.

The evaporation by hot air is best exemplified in the pans of Brame-Chevallier and Péclet. That of the latter is shown in Fig. 222. The evaporating-pan, A, is directly over the fire, the products of the combustion passing by the pipes, B, to the chimney, *g*. The steam from the evaporating-pan passes away through *e*. By means of the axis, *a*, and sieves, *c d*, set in motion by steam-power gearing with *b*, the juice is thoroughly exposed to the blast of hot air generated in C, and passes by the hot pipes, B, into the pan, A. By this constant stirring the juice is prevented from adhering to the pans, and becoming burnt.

FIG. 217.

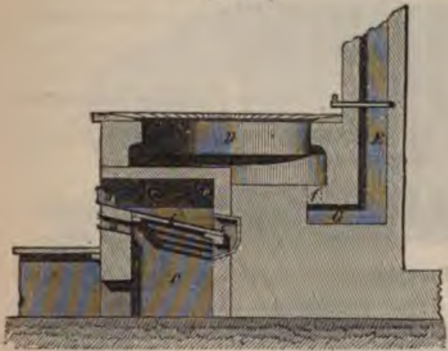


FIG. 218.

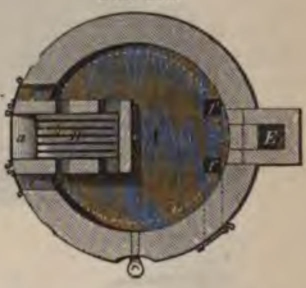


FIG. 219

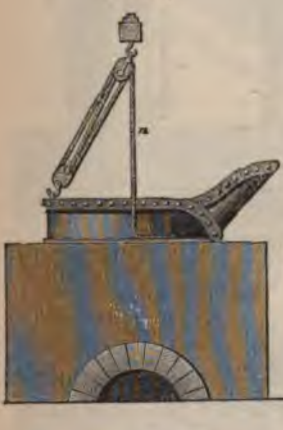


FIG. 220.

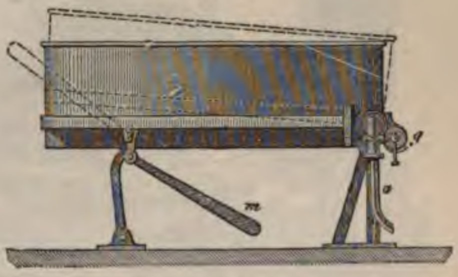
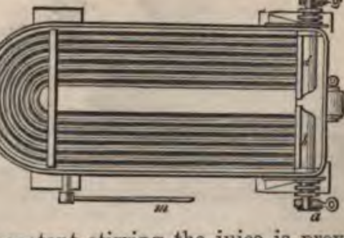


FIG. 221.



Vacuum Pans. An improved evaporation apparatus was invented by Howard, in 1812, in which the juice was placed in chambers of rarified air, or vacuum pans.

The lowest boiling-point of the clear juice in the vacuum pans is 46·1° C.; the usual temperature at which the sugar is boiled 65·5° to 71·1° C.; at a higher temperature the juice loses its power of crystallisation, and forms caramel. The vacuum may be considered as two distinct apparatus:—1. The boiling-pan; 2. The apparatus for exhausting the air and condensing the steam from the juice.

FIG. 222.

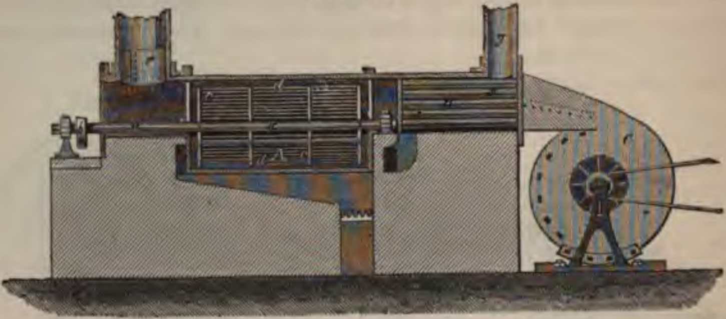
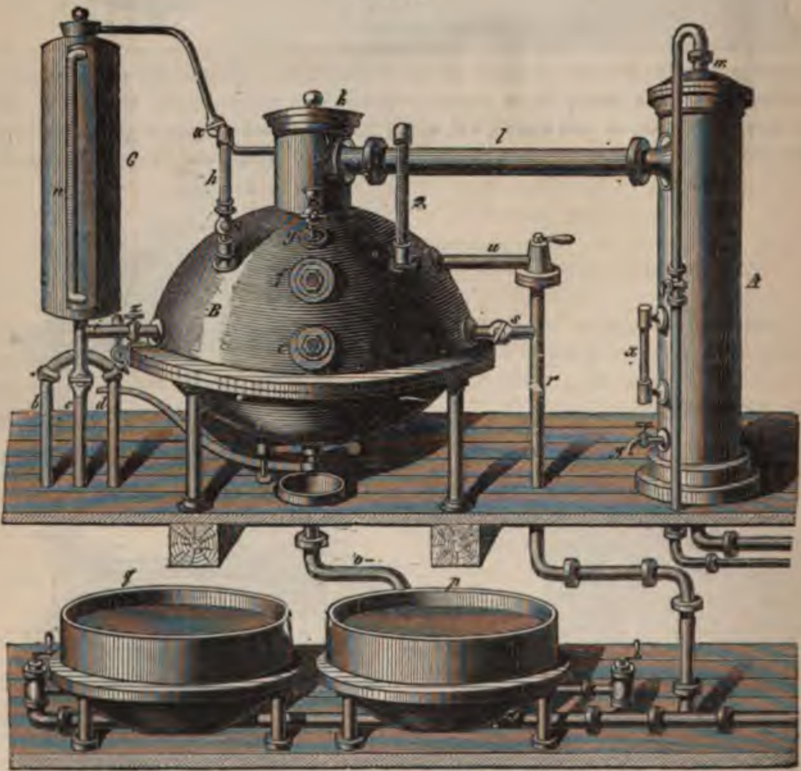
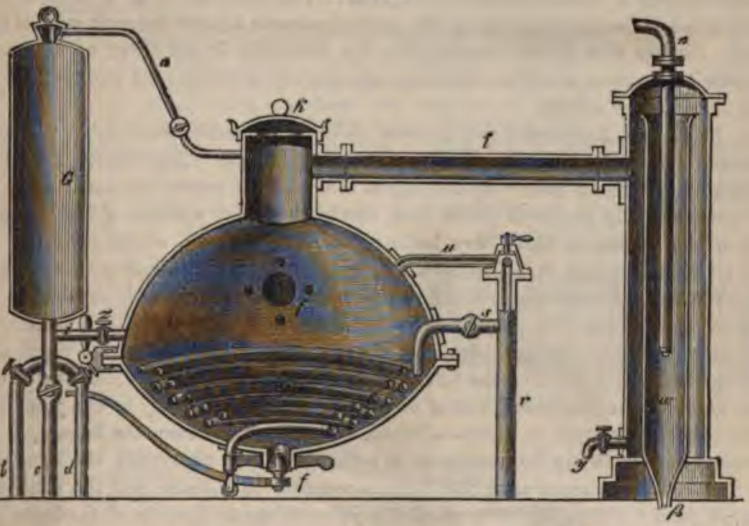


FIG. 223.



In France, Derosne's apparatus is extensively used; but that which we shall describe meets with general approval in Germany, and has the advantages of being simpler in construction and less costly to work. Fig. 223 is a perspective view, and Fig. 224 a section of this form of evaporating pan. The boiling-pan, B, consists of two air-tight hemispheres, surmounted by a funnel connected by the tube, *l*, with the condenser, A. The apparatus is supplied with steam by *r s*, the steam circulating in the boiling-pan by means of the pipes, *g*, Fig. 224. By opening the lever valves, *f*, the juice can be run by means of the pipe, *o*, into the pan, *p*. When the pan, after continued boiling, requires to be re-filled, the pipes *l* and *w* are connected to an air-pump. The manometer, *h*, shows the state of the air-pressure, which can be regulated by opening the pipes connected to the vacuum-chamber. By means of the gauge-cylinder, G, the quantity of syrup in the boiling-pan can be ascertained, the gauge-cylinder being connected to the boiling-pan by the pipes *a* and *i*, and the height read off from the gauge-tube, *n*. The syrup can be removed, for the purpose of ascertaining its consistency, from the gauge-cylinder by means of either of the three pipes, *b c d*. By *u* steam can be admitted to the boiling-pan and condenser. *e* is generally of stout glass, through which the state of the juice can be observed. *g* is the grease-cock, butter or Sostman's paraffin being generally used to prevent the adhesion of the scum to the working parts of the pan, the taps, &c., *f* is the man-hole. The condenser consists of the jacket, B, arranged to prevent the mixing of the juice with the water used for condensation. *x* is the gauge. The pipe *m*, conveying water to the condenser, terminates in a rose. *z* is a thermometer, showing the interior temperature of the boiling-pan.

FIG. 224.



The air-pump being set in operation, the tube *c* is opened, and the gauge-cylinder filled by the juice rising from *q*. By closing *m* and opening *z* the juice is admitted to the boiling-pan. When this is half full the steam-pipe, *s*, is opened, the steam quickly heating the contents of the pan to the boiling-point. The condenser is then placed in working; by opening the pipe, *l*, the steam of the juice passes into the condenser, where it is speedily condensed, passing with the water through β. Trappe's arrangement is sometimes found useful in working the Torricelli vacuum. The condenser is 10·6 to 11 metres above the pan; from it reaches a pipe to a water reservoir beneath, the height of the water in this pipe indicating the degree of rarefaction in the pan.

Evaporating the Juice. Notwithstanding the first purifying, many substances still remain in the juice, the carbonic acid treatment not completely removing the lime, free potassa or soda, ammonia, and nitrogenous organic substances. According to Leplay and Cuisinier, 1000 hectolitres of juice yield 300 kilos. of sulphate of ammonia. Among the former decomposition products are also found nitrate and sulphate of potassa, chloride of sodium, &c., besides levulose, and humus substances, which impart a brown colour to the juice. The clear juice is, therefore, again evaporated to density of 24° to 25° B., and afterwards filtered through animal charcoal. During this second evaporation the ammonia is got rid of, as well as the organic substances, while the filtration removes the alkaline salts and the lime, and also lightens the colour.

5. *Boiling the Evaporated and Filtered Juice to Crystallisation.*—After the second filtering and evaporation the juice is technically termed "thin juice," and is concentrated to "thick juice" by boiling to the point of crystallisation. As a rule, the juice speedily begins to seethe and rise in the usual manner of boiling fluids; but if the throbs in this "dry boiling," as it is termed, sound heavy or dull, "fat" as it is called, it indicates that some quantity of free alkali still is contained in the juice, and a remedy is found in the cautious addition of sulphuric acid. The estimation of the specific gravity of the boiled juice is not practically available as a means of ascertaining the degree of concentration. This is best arrived at by noting the boiling-point of the juice, which varies for pure juice from 112° to 120°; but generally an empirical test is employed, a small quantity of the juice being removed from the pan on a stick of wood, and rubbed between the fingers, a little practice soon enabling the workman to estimate pretty accurately the consistence of the syrup. In some cases the juice is removed in a ladle, and the consistency judged from the tenacity with which the juice clings to the side of the ladle when sharply blown with the breath. The juice when sufficiently concentrated is removed to the cooler to crystallise.

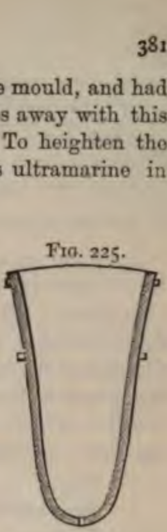
6. *Preparation of Moist or Raw Sugar, and of Loaf Sugar.*—When the juice has been brought to such a degree of concentration that it crystallises on cooling, the final processes commence. The crystallisation proceeds gradually, the crystals forming more quickly the purer the juice. The further the purification has been carried, the easier is the separation of the sugar into molasses, and loaf or crystallised sugar. The loaf sugar is again warmed in a pan and allowed to crystallise in a form to which the general name of sugar-loaf is given, variously distinguished according to their size into—

Loaf form, containing 30 to 34 pounds sugar.
Coarse lump form „ 60 to 70 „
Inferior form „ 120 to 150 „

The forms are generally made of clay, Fig. 225, encircled by a band of wood to preserve the shape. Sometimes the forms are of polished plate iron; *papier maché* has been used with tolerable success for this purpose. By the old method of boiling the sugar in an open pan, the crystals formed unequally in the mould, and had to be removed in several ways. The vacuum pan, however, does away with this process, the sugar crystallising evenly in very large quantities. To heighten the whiteness of the loaf sugar, the manufacturer sometimes adds ultramarine in quantities of 2½ pounds to 1000 cwts. sugar.

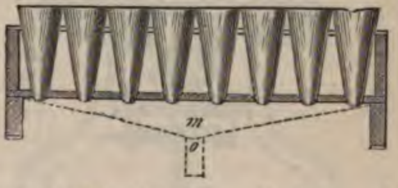
After standing twenty-four hours the sugar is sufficiently set to be removed from the mould. In working on the large scale, the moulds are generally arranged as shown in Fig. 226, the overflowing syrup falling into *m*, whence it is conveyed by *o*. This syrup is known in the trade as green treacle or golden syrup.

FIG. 225.



Draining the Crystals. It is very necessary that all sugars before being moulded should be thoroughly drained from all non-crystallised juice, which would, if allowed to remain, injuriously affect the colour, firmness, and dryness of the sugar loaf. The method of effecting this drying is by first passing a small quantity of water through the sugar; the water combines with a small portion of the sugar to form a very pure syrup, which supplants the molasses or non-crystallised juice in the interstices of the loaf. Practically this filtering takes place in linen cloths, or the form is filled with a layer of pure juice to a thickness of 2 to 3 inches, water being added till a syrup of the consistency of honey is obtained, when the crystallised sugar is forced in, and the form set aside to drain. Lately, a suction apparatus, the invention of M. Kranschütz, has been employed. This apparatus consists of the usual series of forms, to the bottom of each of which is attached a tube proceeding to a vacuum chamber, serving also as a reservoir for the extracted molasses. The vacuum chamber is attached to an air-pump in the ordinary manner.

FIG. 226.



The Centrifugal Drier. The labour and uncertainty attending the above methods of drying have given rise to the invention of a machine by which the non-crystallised juice may be extracted before the sugar is moulded. Schützenbach's machine for this purpose merely consists of a cistern, the bottom of which is formed by fine metal sieves, admitting the percolation of the juice, the damp sugar crystals being removed from the cistern and placed in forms. But the most effective is the centrifugal drier, shown in Fig. 227, the invention of M. Fesca, consisting of an open drum, *a*, of fine meshed wire-work, caused to revolve in the cast-iron case, *b b*, by means of the bevel-wheels, *c d*, gearing with a motive power, the drum making 1000 to 1500 revolutions per minute. The motion of the drum can be stopped by means of the break, *e*, and regulated by the weights placed at *o*. The sugar containing non-crystallised juice is poured into the drum, which being set in revolution, the molasses is, by centrifugal force, driven through the sieve, the dry sugar remaining in masses of 60 to 100 pounds weight. The action of the machine is aided by the cone, *g*. By means of this apparatus, a hundredweight of sugar can be dried in ten to fifteen minutes.

Removing the Sugar from the Form. When all the syrup has been removed, the bottom of the loaf in the form becomes quite dry and hard; the loaf is now loosened in the mould by means of a long knife, so that when the mould is inverted, the sugar-loaf may stand by itself on the "unloading block," as the bench is termed where this operation takes place. From the unloading block the loaf is removed to the drying room, where, first at a temperature of 25° and finally at 50°, it is dried. The loaf is now ready for the market or warehouse. When the pure juice is evaporated to the crystallising point, the small granular crystals formed upon cooling are commercially known as the first product; the syrup removed still contains a quantity of crystallisable sugar, and is further evaporated, the result being known as the second product, and of course considered inferior to the first. In the same way a third and a fourth product, known as after-products, may be obtained. On an average 100 kilos. of beet-root yield:—

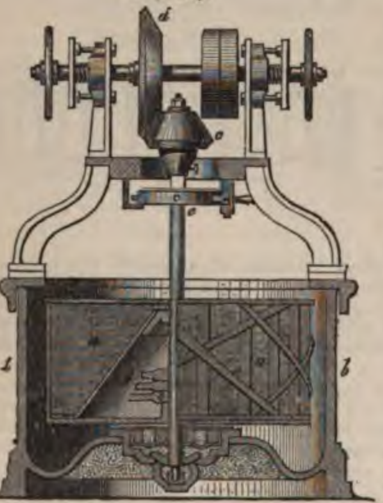
First product at 97 per cent.	5·80 kilos.
Second „ 92 „	2·25 „
Third „ 87 „	0·80 „
	8·85 kilos.
Fourth product, molasses, &c.	3·65 „
Total	12·50

And again, the sugars of each refining is distinguished according to its quality, viz., as refined sugar, lump or boiled sugar, crystallised sugar, raw or moist sugar, and molasses.

Beet Molasses. The molasses so largely formed during the manufacture of beet-root sugar contains most of the foreign substances—caramel, salts, aspartic acid—common to the cane-sugar molasses. Beet molasses is used extensively for sweetening purposes, for the preparation of a coarse spirit, and in many parts of France and Germany as fodder for cattle. The quality depends on the mode of preparing the beet. 100 parts of molasses contain :—

Sugar	50·1	49·0	48·0	50·7
Non-saccharine matter ..	33·3	35·8	34·0	30·8
Water	16·6	15·2	18·0	18·5
	100·0	100·0	100·0	100·0

FIG. 227.



Sugar Candy. The large, hard crystals formed during the various stages of sugar manufacture, are known as sugar-candy. The commercial article is generally obtained from cane sugar, the crystals of beet-root sugar being too long and flat. The amount of sugar-candy made from beet sugar does not exceed 20 per cent. of the entire production. The sugar selected for candy is mixed with 3 to 4 per cent. of animal charcoal, then cleared with white of egg, and filtered. It is next boiled in a copper or an enamelled iron pan over an open fire; whence it is conveyed to a crystallising vessel, the sides of which are perforated with a series of holes, in eight or ten concentric rings, the distance between each hole laterally being less than that between each ring. Through these holes the candy crystallises, the size of the holes being adjusted to the consistency of the boiled sugar by means of a paste made of fine clay, ashes, and ox-blood. The temperature of the drying room is maintained at 75° for six days, when it is reduced to 45° or 50°, and in 8 to 10 days the crystallisation is complete. During the crystallisation the candy must not be moved or shaken, or the air allowed to affect it. Upon the completion of the crystallisation, the candy is found covered with a mixture of syrup and small crystals; these are removed by filling the crystallising vessel with weak lime-water. The rinsing water must be lukewarm, as cold water cracks the crystals, and hot water makes them, as it is technically termed, blind. The crystallising vessel, when emptied of the rinsing water, is soaked to remove all saccharine matter, and if this be not effected with hot water, a smooth stone is used to knock away the adhering crystals. After standing a day to dry, the sugar candy is ready for the market. It is commercially known as of three kinds:—the finest, refined white, has a large colourless crystal; yellow candy, a straw-coloured crystal; and brown candy is similar in colour to ordinary moist sugar. In some parts of France a dark candy is manufactured under the name of *Sucre de Boerhave*. Inferior cane sugar is employed for the brown, boiled sugar for the yellow, and refined sugar for the white candy. Sugar-candy is extensively used, the white principally in preparing "Liqueur," a solution of candy in wine or cognac, also in champagne manufacture, and in all cases where a clear sweetening solution is required in large quantities. The yellow candy is used for sweetening tea and coffee in restaurants, and enters largely into the recipes of the pharmaceutist for affections of the throat and chest, as well as for making syrups intended as vehicles for nauseous medicines.

The total annual production of beet-root sugar amounted in 1870 to 16,000,000 cwts., of which 6,000,000 cwts. are due to France.

Grape Sugar.

Grape Sugar. Grape sugar, potato sugar, starch sugar, glucose, or dextrose, is a sugar crystallisable with difficulty, occurring in a non-crystallised state as levulose or chylariose (γυλαριον, syrup) in many sweet fruits, in the vegetable kingdom, and it forms the solid crystalline portion of honey. It may be obtained by any of the following processes:—

a. By the conversion of starch, dextrine, cane sugar, or some gums by means of dilute acids or diastase.

b. By treating cellulose and similar vegetable matters with dilute acids.

c. By decomposing organic substances, such as amygdalin, salicin, phloridzin, populin, quercitrin, gallo-tannic acid, &c., that by treatment with dilute acids or synaptase (emulsin) are separated into grape sugar and other substances.

Grape sugar is found in the various fruits in the following quantities:—

	Per cent.
Peach	1·57
Apricot	1·80
Plum	2·12
Raspberry	4·00
Blackberry	4·44
Strawberry	5·73
Bilberry	5·78
Currant	6·10
Plum	6·26
Gooseberry	7·15
Cranberry	7·45 (according to Fresenius).
Pear	8·02 to 10·8 (E. Wolff).
Apple	8·37 (Fresenius).
"	7·28 to 8·04 (E. Wolff).
Sour cherry	8·77
Mulberry	9·19
Sweet cherry	10·79
Grape	14·93

Grape sugar, $C_6H_{12}O_6,H_2O$, crystallises from its aqueous solution in granular, hemispherical, warty masses. It is less easily soluble in water than cane sugar, and requires 1½ of its own weight of cold water, while in boiling water it is soluble in all proportions, forming a syrup possessing but poor sweetening qualities. There are required 2½ times more grape sugar than cane sugar to sweeten the same volume of water. At 120° grape sugar loses its water, and has the formula $C_6H_{12}O_6$. At 140° it is converted into caramel. Heated with caustic alkalies melassic acid is formed, together with humus-like substances. Treated with sulphuric acid, grape sugar forms sulpho-saccharic acid, and with common salt a soluble compound of sweetish saline taste. With caustic potash in excess a grape sugar solution, when heated to the boiling-point, reduces the hydrate of oxide of copper to suboxide, oxide of silver to metallic silver, and chloride of gold to metallic gold. A mixture of ferridcyanide of potassium and potash with the aid of heat decomposes grape sugar and discharges the original yellow colour of the fluid. Under the influence of a ferment grape sugar suffers many changes, the product varying with the ferment and method of treatment employed. Beer yeast decomposes grape sugar into alcohol and carbonic acid.

100 kilos. of grape sugar give:—

Alcohol	51·11
Carbonic acid ..	48·89

There are also found under certain conditions of temperature and concentration the homologues of alcohol, viz., propylic alcohol, butylic alcohol, and amylic alcohol, and under all conditions glycerine and small quantities of succinic and lactic acids. When fermentation is effected in the presence of alkaline reagents, lactic acid is formed without any disengagement of gas. Ordinarily the formation of lactic acid is merely a stage in the process of conversion, the lactic acid decomposing into butyric and acetic acids with development of hydrogen. Under certain conditions mannite may be prepared from grape sugar; several other gum-like substances may also be obtained. If to a grape sugar solution a small quantity of caseine and of carbonate of lime be added, and the mixture submitted to a temperature of 90°, butyrate of lime will be thrown down after fermentation, carbonic and hydrogen gases being continuously evolved.

Preparation of Grape Sugar. Grape sugar may be prepared from:—

a. Grapes.
b. Starch.
c. Wood and similar vegetable substances.

When grape sugar is prepared from the grape, the juice of the white grape is preferred, and set aside to clear. The cleared must is heated to the boiling-point with pieces of marble, chalk (not with burnt lime), or witherite (carbonate of baryta) to neutralise a portion of the tartaric acid. It is then allowed to stand for twenty-four hours, and during this time the insoluble salts of lime are deposited. The must is now cleared with ox blood in the proportion of 2 to 3 litres of blood to 100 litres of must, and next evaporated to 26° B. After remaining a short time in a tub to clear, the impurities are removed, and the must again evaporated—this time to 34° B. By these means a syrup is produced, from which the grape sugar can be immediately obtained. The syrup is concentrated by boiling and run into crystallising vessels, where after three to four weeks the sugar crystallises out; it is separated from the non-crystallised chylariose in a centrifugal machine. For experimental purposes the crystals may be separated by placing the concentrated syrup on a heated porcelain or glass plate.

1000 parts by weight of grapes give:—

Must	800
Syrup	200
Raw grape sugar ..	140
Pure grape sugar ..	60—70

The preparation of grape sugar from starch is an important branch of the sugar-boiler's art. Dilute sulphuric acid and the fecula of potato starch are the active agents. The principal processes are the following:—

a. The boiling of the starch-meal with dilute sulphuric acid is effected on a small scale in leaden pans, but in an extensive preparation iron pans are employed. The requisite quantity of water is first heated to the boiling-point, and to this is added the sulphuric acid diluted with 3 parts by weight of water. The starch is also previously brought by the addition of water to a milky consistency. The liquids so prepared are mixed, and the boiling continued until all the starch is converted into sugar. An intermediate stage, not usually noticed by the manufacturer, is the conversion of the starch into dextrine, which in its turn suffers conversion into grape sugar. The entire conversion of the dextrine into grape sugar cannot be ascertained with certainty by the iodine test, as sometimes a purple-red tint is produced, while in others there is no change. The most reliable test is that with alcohol, founded on the known insolubility of dextrine in an alcoholic menstruum. To 1 part of the solution to be tested there are added 6 parts of absolute alcohol; if no precipitate is thrown down there is no dextrine remaining, and the conversion has been entire. The proportions of the materials are generally to 100 kilos. of starch meal—2 kilos. of ordinary sulphuric acid of 60° B. and 300 to 400 litres of water.

The conversion of the starch into grape sugar is hastened by the addition of a small quantity of nitric acid.

b. The separation of the sulphuric acid from the sugar solution is a most important operation, for the colour, purity, and flavour all depend upon success in this stage of the process. The acid is neutralised by baryta or by lime, with either of which it forms an insoluble salt, deposited at the bottom of the neutralisation vessels, and leaving a clear supernatant syrup. The baryta can be employed as carbonate (witherite), and is without doubt the better neutralising agent, sulphate of baryta being very insoluble. Lime, although ordinarily used, forms with the sulphuric acid a sulphate (gypsum) that is not perfectly insoluble in water. It can be employed either as marble, chalk, or caustic lime. The neutralisation is completed in the boiling-pan while the sugar solution is still hot. For every kilo. of sulphuric acid (technical atomic weight = 100 to 106) so much pulverised marble (chemical atomic weight = 100) is required as the varying strength of the acid may demand. After the addition of the marble powder, and when the effervescence has subsided, the liquid must be tested with litmus paper, or, better, with tincture of litmus; if the sugar solution be neutralised when at 26° B. density, the following evaporation will concentrate even the smallest quantity of sulphuric acid which may have remained, and render another neutralisation necessary. To ensure perfect neutralisation it is useful to add an excess of carbonate of baryta in the proportion of 250 to 500 grms. to every 10 kilos of sulphuric acid.

c. Evaporating and Purifying the Sugar Solution.—This part of the process is accomplished first in a copper pan over a slow fire, or better, by heating with steam. The impurities separate and are absorbed in the scum, which is removed by means of ladles. The evaporation is continued until the syrup marks 15° to 16° B., when it is passed through a filter, generally of animal charcoal. It is then removed to a large reservoir, and, if a granular sugar be desired, evaporated to 40° to 41° B., in flat pans, from which it is taken to be placed in the crystallising vessels. These vessels are provided at the bottom with twelve to twenty-four holes, into which wooden plugs are fitted, by removing which, when the sugar has crystallised, the molasses are removed. The crystals are dried, sifted, and either pressed into sugar-loaf forms or packed in casks. The crystallisation is effected in eight to ten days.

The manufacture of grape sugar from wood and similar vegetable substances is only of value in relation to the production of spirits, and recently as a by-process of the manufacture of paper from wood.

Composition of Starch Sugar. The composition of starch sugar as it occurs in commerce is very varied. During inferior seasons the marketable starch sugar may contain 50 per cent. sugar, 32·5 per cent. foreign substances, and 17·5 per cent. water. G. Schwaendler found by the analysis of various samples of last year's (1870) sugar the following percentages:—

	1.	2.	3.	4.	5.
Grape sugar	67·5	64·0	67.2	75·8	62·2
Dextrine..	9·0	17·4	9·1	9·0	8·8
Water	19·5	11·5	20·0	13·1	24·6
Foreign substances ..	4·0	7·1	3·7	2·1	4·4
	100·0	100·0	100·0	100·0	100·0

Uses of Grape Sugar. The sugar prepared from starch, in addition to the sugar yielded really by the grape, is largely employed in wine-making and in the brewing of beer. In the latter case the grape sugar is prepared by means of diastase; that its use is extensive may be gathered from the fact that to 3 cwts. of malt 1 cwt. of potato sugar is employed. It is also employed instead of honey in confectionery, for colouring liquors and vinegars brown, in rum and cognac, beer and wines. In the latter cases it is known as *sucre couleur*, being then a grape sugar that has been re-melted, sometimes with the addition of carbonate of soda or caustic soda to deepen the colour.

FERMENTATION.

Fermentation. Fermentation is a term applied to the peculiar changes of complex organic substances of the amylaceous and saccharine type under the influence of certain putrescible nitrogenous substances or ferments. The decomposition of fermentable organic bodies by a ferment effects the separation of their constituents into two or more combinations, as when by a yeast-ferment dextrose and levulose are converted into alcohol, its homologues, and carbonic and succinic acids; or the molecules of the original substances are re-grouped, as in the conversion of sugar of milk into lactic acid during lactic acid fermentation; finally, the elements of the organic substance may enter into combination with the oxygen of the atmosphere either to form new organic combinations, or to separate into its inorganic constituents carbonic acid, carburetted hydrogen, &c. This latter decomposition is termed *mouldeirng* when a residue rich in carbon (humus) remains, but when only the mineral constituents remain, *decay* is said to have been reached. These terms are thus defined more by custom or usage than by direct etymology—dictionaries hardly distinguish between them, but the difference is known to all. If large quantities of water be present both these processes are resolved into *putrefaction*, in which chiefly gases carbonic—acid, ammoniacal, sulphuretted hydrogen—and water are disengaged. But fermentation always results in the remaining or the formation of other organic compounds, and the variety of fermentation set up mostly depends on the state of decomposition of the azotised matter employed as a ferment. The most important ferment is undoubtedly yeast, but the ferment may be either an organic substance (yeast) or a protein body in a putrescent state—it is always a nitrogenised body. In a technological work the varieties of fermentation may be classed as—

1. Vinous or alcoholic fermentation, including the changes observed during the processes of wine-making, beer-brewing, and the production of alcoholic liquors or spirits.

2. Lactic acid fermentation, taking place during the souring of milk; and at a higher temperature changing to
3. Butyric acid fermentation.

To these fermentations may be added—

4. Putrescence, noticeable only in technological chemistry as a stage to be most carefully avoided.

Vinous Fermentation. Vinous or alcoholic fermentation is the result of the decomposition of saccharine matter, dextrose or glucose, levulose or chylariose, and lactose into several products, principally alcohol and carbonic acid. According to the recent researches of Lermer and Von Liebig (1870) dextrine in the presence of sugar is converted into equal parts of alcohol and carbonic acid. This will be seen from the following table, which gives the result for 100 parts by weight:—

		Alcohol.		Carbonic Acid.		
Crystallised dextrose,	$C_6H_{14}O_7$,	46·40	+	44·40	=	90·86.
Anhydrous dextrose,	$C_6H_{12}O_6$,	51·10	+	48·90	=	100·00.
Cane-sugar,	$C_{12}H_{22}O_{11}$,	53·80	+	51·46	=	105·26.
Starch-meal,	$C_6H_{10}O_5$,	56·78	+	54·32	=	111·10.

$$1 \text{ mol. dextrose, } C_6H_{12}O_6 = 180, \text{ gives } \begin{cases} 2 \text{ mols. alcohol, } 2C_2H_6O & = 92 \\ 2 \text{ mols. carbonic acid, } 2CO_2 & = 88 \end{cases}$$
$$\overline{180}$$

Recently Pasteur has shown that lactic acid does not result from alcoholic fermentation, but that succinic acid is a constant product of this fermentation in quantities never less than 0·6 to 0·7 per cent. of the weight of the sugar employed. Glycerine is another constant production to the extent of 3 per cent. of the sugar; this substance occurs in all wines. The 5 to 6 per cent. of substances remaining may therefore be thus divided:—

Succinic acid	0·6 to 0·7
Glycerine	3·2 to 3·6
Carbonic acid	0·6 to 0·7
Cellulose, fatty substances, &c.	1·2 to 1·5
	5·6 to 6·5

Yeast. The nature of alcoholic fermentation was first investigated by Cagniard-Latour, while our present knowledge is due chiefly to the researches of A. de Bary, J. Wiesner, Hoffman, Bail, Berkley, Pasteur, Hallier, Béchamp, Lermer. Yeast on being introduced into a fermentable fluid rapidly throws out fermenting arms, as it were, until the fluid is covered with a *superficial* ferment, termed in German the *Oberhefe*, while at the bottom of the vessel a viscid sediment is deposited, known in German as the *Unterhefe*. The oberhefe or superficial ferment, is employed as *barm* by the baker, for the purpose of leavening his bread; while the unterhefe or sedimentary ferment is that employed in the fermentation of wines and of Bavarian beers; these beers differ from the general beers of England, France, and Germany, in not souring by exposure to air, this quality being due to the peculiarity in the process of fermentation, *Untergahrung*, or fermenting from below, during which the gluten, the substance absorbing the oxygen of the air, is removed. In the distillation of brandy, the yeast employed is a mixture of *barm* and *bottom* yeast, as the terms run in this country. Fresh yeast appears as a grey-yellow or red froth of strong odour, and with an acid reaction. Under the microscope the two kinds of yeast are easily distinguished. The superficial yeast or barm consists of globular or ellipsoidal cells of equal size, and about 0·01 millimetre diameter. They float partly alone, partly in groups in the fluid. The walls of the cells are so transparent that the inner cells can be seen through the upper. In the centre of each cell appears a dark speck or grain, the *protoplasma*, sometimes consisting of more than one grain. The bottom yeast or sedimentary ferment also consists of cells, but these do not cling together so tenaciously as the cells of the barm, and are generally isolated, while the adhesion is merely mechanical between those that do cling together, a slight concussion being sufficient to effect their separation. Sometimes a large cell of the bottom yeast contains two, three, or even four smaller cells, the dimensions of these cells varying greatly, and not being nearly so constant as in the cells of the barm.

"I found," says Dr. Wagner, "from the researches of Mitscherlich, communicated to the Philosophical Faculty of the University of Leipsig, that the sprouting or transplanting of the cells had been actually witnessed under the microscope—that a parent cell had been observed to put forth little cells, which gradually grew in size. These observations had been made with barm or superficial yeast, and I wished to ascertain if the cells of the bottom yeast or sedimentary ferment were propagated in the same manner. For this purpose I placed a sedimentary yeast-cell, containing a germ, under the microscope in a bath of concentrated beer-worts. The temperature varied between 7° to 10°. The cell remained unaltered for some time, but finally there appeared 30 to 40 small cells. These cells were either separated from the mother-cell by the bursting of the cell walls, or had been introduced as spawn into the field of the microscope in the beer-worts; which was the true case the microscope could not reveal, for no separated spawn were visible. An analysis of the two yeasts gave:—

	Barm.	Sedimentary Yeast.
Carbon	44·37	49·76
Hydrogen	6·04	6·80
Nitrogen	9·20	9·17
Oxygen, sulphur, and ash	40·38	34·26

"The barm contained 2·5 per cent., the sedimentary yeast 5·29 per cent. of ash. The amount of sulphur was 0·5 to 0·8 per cent. The ash consisted essentially of potash, phosphoric acid, silica, and magnesia."

According to the recent researches of Liebig, Pasteur, Lemaire, and others, alcoholic fermentation is essentially due to the formation of yeast-cells, and to the development of organic substances. There are two cases to be considered. Yeast, with its botanical names, *Saccharomyces cerevisiæ*, or *Hormiscium cerevisiæ*, a descendant of the fungi, *Penicillium glaucum*, *Ascophora Mucedo*, *A. elegans*, and *Periconia hyalina*, the spawn of which is always occurring in the atmosphere, ferments either with a pure sugar solution, without the existence of protein substances, or in the presence of albuminous substances. The latter case occurs also when a solution of sugar containing an albuminous body is so situated as to be partially or wholly open to atmospheric influence. The local ferment floating in the air in the shape of yeast-spawn finds in this solution a ready agent for its extension. But in the first case, where the sugar solution is mixed with the yeast, without the necessary protein substance as food or nourishment for the cells, the fermentation is after a time exhausted, and is not again set up. It is for a similar purpose that during the process of brewing the yeast cells are fed with a substance formed in the germination of barley. During this germination the gluten of the seed passes over into diastase, of all nutriment that upon which the yeast cells flourish best.

The nature of the yeast cell is a most interesting question. Is it more nearly allied to the animal or to the vegetable kingdom? The line of demarcation is not always definite, yet there would appear some interesting analogies that should not be overlooked. "Plants," says Professor Williamson, "build up complex substances from simple. All the most complex substances that we can get are made in the organisms of plants. They may have been taken over by animals from plants, but they are formed in the main by plants. And the chief chemical activity of animals is precisely opposite; they take those complex substances and break them down, by means of their vital functions, to the simple products which are exhaled and given off in the processes of animal life. Therefore, the question whether the process which the yeast carries on is a synthetical process—a building up—or whether it is in the main an analytical process, is certainly one of the most important which can guide us. From what we know best regarding the nature of the yeast cells, the food which we know they take in large quantities, and upon which they thrive, is certainly exceedingly complex, and the products which they give off are exceedingly simple in comparison. Their functions are in the main (those which we know best at any rate) analogous to those which take place in animal organisms, and are most remote from those which take place in vegetable organisms."

Among the most remarkable decompositions effected with the aid of yeast cells are those described by Liebig in a recent paper, in which it is stated that yeast cells will assimilate tartaric acid, malic acid, and nitric acid; the latter it deprives of a portion of its oxygen, converting it to nitrous acid.

Conditions of Alcoholic or Vinous Fermentation.

The conditions of alcoholic fermentation are the general conditions of the vegetation of the yeast plant, with the distinction that by vinous fermentation the largest amount of alcohol is obtained. The following conditions must be fulfilled when alcoholic fermentation is the desideratum:—

1. *An aqueous solution of sugar*, in the proportion of 1 part of sugar to 4 to 10 parts of water. The sugar can be employed as grape sugar, dextrose, or levulose, which is always capable of fermentation, or an unfermentable sugar, cane sugar, or sugar of milk, may be converted by means of an acid or suitable agent into fermentable sugar. However gradual the process may seem, cane sugar is always converted into grape sugar before fermentation sets in.

2. *The presence of yeast, or spawn.* In the first case, 1 part of yeast to 5 parts of sugar is sufficient to effect a strong fermentation. If spawn only is present, there must also be present substances upon which the spawn may feed or develope—protein substances, phosphoric acid, humus, and alkalies. If no ferment exists, the only other condition under which fermentation is effected is by exposure to—

3. *The atmosphere*, which introduces the before-mentioned ferment and furnishes life.

4. *A known temperature*, the limits of which are 5° and 30° C. As a rule vinous fermentation is effected between 9° and 25°. The lower the temperature the longer the time required for the fermentation to subside, and conversely. At 30° and at higher temperatures, the vinous fermentation easily goes over into butyric acid fermentation. The making of wines is based on a practical acquaintance with alcoholic fermentation; but in this case only a portion of the sugar of the must goes over into alcohol and carbonic acid. The alcohol remains, while the greater part of the carbonic acid escapes.

In beer-brewing the substance forming alcohol is mostly starch, part of which goes over into unfermentable dextrine, but the greater into easily fermentable dextrose. It is arranged that the beer shall hold a small portion of the dextrose unchanged until the after-fermentation at a lower temperature, during which much of the carbonic acid is expelled, the alcohol remaining in the beer.

In the brewing of beer, only a part of the raw material or starch employed goes over into dextrose, and finally into alcohol and carbonic acid; but in the manufacture of spirituous liquors the given material—starch or sugar—is converted into the greatest possible quantity of alcohol in the shortest time, and afterwards separated by distillation. The aim of the wine maker is, of course, to produce the greatest quantity of wine; of the brewer, the maximum amount of beer; and of the distiller, the largest yield of spirit. The residue from the distillation of spirits is often employed in making concentrated food for animals.

In the baking of bread and confectionery the lightening or leavening of the dough is effected by alcoholic fermentation, but only the carbonic acid, and not the alcohol, is of use. In the foregoing illustrations of the application of fermentation, it will have been perceived that the object is the generation of alcohol or of carbonic acid, or of both, according to the requirements of the case. The particulars we will consider under separate divisions.

WINE-MAKING.

Wine. By the name of wine is generally distinguished an alcoholic fluid prepared without distillation by the fermentation of grape-juice. In the widest meaning of the term is included the result of the vinous fermentation of all natural juices.

The Vine and its Cultivation. The vine, *Vitis vinifera*, is generally cultivated in Europe at a temperature of 50°, while the best and ripest drinking wines are obtained from grapes grown at a temperature of 51° to 52°. It requires an average temperature of 10° to 11°, and an average summer temperature of 18° to 20°; but it is the summer's sun that forms the sugar. A climate with severe winters and hot summers is therefore as favourable to the cultivation of the grape as a temperate climate. England, with a mean average annual temperature of 11°, is consequently very unsuited to the growth of the vine. The weather has the greatest influence upon the vine: during the growth rain is required, but during the ripening only the sun's rays should reach the grape. The soil is not so much a matter of consequence if a quantity of potash be present; but a warm, loose soil is the best. Clay shale, clay marl, gypsum, lime, and chalk formations are very suitable to the vine. The uses of the grape are numerous in the highest degree; it serves chiefly in the preparation of must for wine, the preparation of grape sugar, French brandies or cognacs, wine-vinegars, &c. Oil is prepared from the seeds, and the lees are burnt for their potash.

Vintage. The sugar is found at an early stage of the growth of the grape. When unripe the grape contains malic, citric, and tartaric acids, bitartrate of potash and lime, organic salts in smaller proportions, and a little colouring and extractive matters. Successive analyses have been made of the grape during its period of growth by C. Neubauer, from samples obtained from the Neroberg, near Wiesbaden (1868), and have given the following results:—

July 27th ..	0·6	per cent.	Sugar and	2·7	per cent.	free acid.
August 9th ..	0·9	,,	,,	2·9	,,	,,
,, 17th ..	2·3	,,	,,	2·8	,,	,,
,, 28th .	8·2	,,	,,	1·9	,,	,,
September 7th	11·9	,,	,,	1·2	,,	,,
,, 17th	18·4	,,	,,	0·95	,,	,,
,, 28th	17·5	,,	,,	0·8	,,	,,
October 5th ..	16·9	,,	,,	0·8	,,	,,
,, 12th..	18·6	,,	,,	0·9	,,	,,
,, 22nd	17·9	,,	,,	0·9	,,	,,

It appears that the riper the grape the more sugar it contains, and it produces a wine richer in alcohol, so that the grapes are never gathered until perfectly ripe. The grapes of the white vine are of a brown-yellow when ready for gathering for wine, and the red and blue grape must be extremely dark before the seed will separate from the fleshy part of the grape sufficiently for wine-making purposes.

The grapes are sometimes plucked, and sometimes left on the stalk. The separation of the grape from the stalk is effected either by hand or by the aid of a hurdle, the openings between the bars of which are only sufficiently wide to admit of the passage of the grape, or by a wooden or brass trellis-work, or finally with a large wooden fork 0·5 to 0·6 metres in length. The stalk contains much tannic acid, and it is therefore necessary that all the grapes should be thoroughly separated before pressure; but in some cases when the grape contains too little of this acid, a few stalks are purposely allowed to remain.

The Pressing of the Grapes. After the grapes are stripped from the stalks, they are placed in a vat and stamped with a wooden maul or pestle to express the juice. They are generally allowed to remain for some time, and afterwards submitted to a second bruising, the maceration being for the purpose of softening the skins and fleshy part of the grape. The whole of the juice and grape-skins, or marc, is then put into a butt with perforated sides, through which the must trickles into the fermentation vat beneath. If a white wine is being operated upon, to prevent it becoming *stringy*, as the term runs, from an insufficient supply of tannic acid, small quantities of stalks are added from time to time. This addition renders the wine more easily clarified by the addition of white of egg or isinglass in a subsequent stage of the process. While the wine is in the vat, the fermentation is allowed to proceed, and the slight acidity generated reacts upon the colouring matter and aromatic constituents of the grape, these being taken up in the alcohol set free.

The wine-presses are of very various construction. The most general is the beam-press, roughly constructed with a pole 12 to 16 metres in length, and four to six oaken cross beams. These presses have considerable power, but they are tedious to work, and soon get dirty. The lever-press is more efficacious, and is made in many forms, the pressure being mostly from below. The hurdle- or sledge-press is of the rudest kind, consisting merely of hurdles and rough heavy stones. The best presses are the screw-presses made of wood or cast iron. 100 parts of grapes yield 60 to 70 parts of must. The ripest grapes yield the first juice in the press; the results of stronger pressure are more acid. The result of the first pressure is termed the wine or the first wine; then comes the press wines; and finally the after wines. The residue or marc is sometimes treated with water to obtain an inferior wine.

The Centrifugal Machine. In 1862 Steinbeis, of Stuttgart, with the co-operation of Reihlen, endeavoured to express the juice of the grape with the aid of the centrifugal machine instead of the press. They were enabled in ten minutes to express the juice perfectly from 100 to 120 pounds of grapes, including the time required to fill and empty the machine. In 1869, Ballard and Alcan obtained equally successful results, some of which were made comparative with those obtained by a good press:—

	Centrifugal Machine.	Press.
Must	79·141	77·086
Residue	20·214	18·601
Loss	0·645	4·313
	100·000	100·000

Chemical Constituents of the Must. Besides the stalk of the grape, there are the outside skin, the hull, the seeds, and the juice. Of the composition of all these substances, with the exception of the grape juice, our knowledge is very deficient. Besides cellulose, the stalks contain much tannic acid, and an acid very sour to the taste. The hull of the grape contains the colouring matter and a small quantity of tannic acid. The seed contains a peculiar acid, œnanthic acid, and an ether, bearing the same name, to which the bouquet of the wine is due.

The Sugar of the Grape. The wine grape contains more sugar than any other kind of grape. The quantity of sugar—a mixture of dextrose and levulose—is seldom [illegible] than 12 per cent., while it is sometimes as much as 26 to 30 per cent. The proportion of acid to sugar is in good years and in a good grape, according to Fresenius, 1 : 29; in average years and cases, 1 : 16; and when the proportion is only as 1 : 10, the grapes are useless for the production of wine. The proportion between the acid and sugar in wine-must from the same kind of grape for different years is, according to this eminent chemist:—

In a very inferior year, 1847, as 1 : 12
In a better year, 1854, ,, 1 : 16
In a good year, 1848, ,, 1 : 24

During the fermentation of the must, bitartrate of potash is deposited, and from this source most of the tartar of commerce is obtained. This salt is insoluble in dilute alcohol; consequently as the sugar changes into alcohol it is thrown down. It is from the fact of containing tartaric acid, which, by combining to form an insoluble salt, is thus prevented exerting an unfavourable influence on the wine, that grapes possess so much the property in proportion to other fruits of making a good wine. The malic and citric acids contained in currants and gooseberries cannot be withdrawn in this manner: hence the addition of sugar to wines made from these fruits to veil the acidity; the addition, however, giving rise to the danger of a second fermentation, and consequent acidity. According to Al. Classen, 1 kilo. of ripe grapes gave (in 1868) 577 to 688 grms. of juice; and 1 litre of juice contained:—

Water	860 to 830 grms.
Sugar (dextrose and levulose)	150 ,, 300 ,,
Pectin, gums, extractive matter, Protein substances, organic acids, and mineral matters	30 ,, 20 ,,
	1040 to 1150 ,,

1000 parts of juice of ripe (Rhine, 1868) grapes contained:—

	1.	2.	3.
Solid matter	164·4	189·7	204·6
Sugar	149·9	162·4	174·0
Free acid..	7·2	6·8	4·8
Ash	2·7	3·0	4·0

In 100 parts of the ash were contained:—

	1.	2.	3.
Phosphoric acid .. .	16·6	16·1	14·0
Potash	64·2	66·3	71·4
Magnesia	4·7	2·8	2·6

C. Neubauer (1868) analysed two kinds of grapes, and found—

	Neroberger (large grapes).	Steinberger (selected grapes).
Sugar	18·06	24·24
Free acid	0·42	0·43
Albuminous substances	0·22	0·18
Mineral constituents (potash, phosphoric acid, &c.)	0·47	0·45
Combined organic acids and extractive matter	4·11	3·92
Total of soluble constituents	23·28	29·22
Water	76·72	70·78
	100·00	100·00

The Fermentation of the Grape Juice. The fermentation of the grape juice is spontaneous; that is, it is consequent upon the exposure of the grape juice to the atmosphere, without the addition of yeast. The albuminous matter of the must forms, under the influence of the atmospheric spawn or yeast germ, the well-known fungus *Penicilium glaucum*, or yeast cells. The fermentation begins at a temperature of 10° to 15°, and is effected more or less rapidly according to the temperature. Too low a temperature will retard the progress of fermentation, as also will the addition of sulphurous acid; the same effect is obtained by the addition of other sulphur compounds, as, for instance, the essential oil of mustard, which contains sulphocyanide of allyl. The must is left in open vats; bubbles of carbonic acid soon appear, scum collects upon the surface of the juice, and an alcoholic odour pervades the wine at this stage. About the seventh day the fermentation commences to decrease, and about the tenth or fourteenth day the fluid begins to clear, no more carbonic acid or scum appearing. The yeast cells formed are carefully removed from the bottom of the vessel, and the wine run into casks, where it undergoes a slight after-fermentation. If there be much sugar contained in the grape, and a small quantity of azotised matter, the resulting wine will be sweet; but if the proportion of sugar be small and albumen large, a dry wine is the result.

Drawing off and Casking the Wine. After the principal fermentation the greater part of the sugar of the must is found to be separated into alcohol and carbonic acid. There is still likely to arise, unless the temperature be considerably decreased, a fresh fermentation, known as the after-fermentation. Should this after-fermentation continue too long, vinegar is formed, and to prevent this, the wine, after the disappearance of the bubbles of carbonic acid upon the conclusion of the principal fermentation, is at once "spigotted off" from the lees into casks, the object being to cut off communication with the atmosphere as much as possible. The casks are nearly filled, and are bunged loosely, being filled completely a day or two after. Wines casked in December will often continue fermenting till February or March. Strong wines rich in alcohol can be kept in cask until they have become quite clear; but weak wines must be soon bottled, as the oxygen of the air is liable to convert the hydrate of the oxide of ethyl or alcohol into trioxide of acetyl or vinegar.

Constituents of Wine. Constituents that were not found in the must are characteristic of the wine—the chief of these is alcohol. Succinic acid and glycerine, the constant products with alcohol and carbonic acid of vinous fermentation, are also to be found. A "dry" wine, such as the French and Rhenish wines, is one in which all the sugar has been decomposed; a "sweet" wine, on the other hand, is one in which some sugar has remained undecomposed either from an insufficiency of albuminous matter to nourish the yeast cells, or from the checking of the fermentation by exposure to a low temperature. A very sweet and thickly fluid wine is termed a "liqueur." The difference in colour is due to three substances—a blue colouring matter, a brown colouring matter, and tartaric acid. The brown colouring matter is present in all light or white wines, while the blue colouring matter, found in the skins of purple or black grapes, is in the wine a red colour, the change arising from the contact with the tartaric acid. Wines of the first year after growth are termed new or "green" wines. The average composition of wines, in 1000 parts, is the following:—

Water	900—891
Alcohol*	80—70
Homologues of alcohol (propylic, butylic alcohol)*	20—30
Ethers (acetic, œnanthic)*	
Essential oils	
Grape sugar (dextrose and levulose)	
Glycerine*	
Gums	
Pectin	
Colouring and fatty substances	
Protein bodies	
Carbonic acid*	
Tartaric and racemic acids	
Malic acid	
Tannic acid	
Acetic acid*	
Lactic acid (?)*	
Succinic acid*	
Inorganic salts	

Those substances marked (*) are formed during the principal fermentation.

The quantity of alcohol contained in a wine is due partly to the quantity of sugar and partly to the quantity of albuminous matter contained in the must. It is chiefly ethylic or ordinary alcohol. The specific weight of the wine gives only approximately the alcoholic contents; a better method of estimation is by means of an alcoholometer. Of these instruments, Geissler's Vaporimeter is, perhaps, one of the best, in which the pressure exerted by the vapour of the wine upon a column of mercury gives a measure of the alcohol contained. The vapour of absolute alcohol at a temperature of 78·3° exerts a tension equal to that exerted by aqueous vapour at 100°. It is therefore only necessary to ascertain the height of the column of mercury and the temperature to arrive at the quantity of alcohol. The apparatus is shown in Fig. 228, and consists essentially of four parts, viz.—1. A brass vessel, A, half-filled with water, heated by means of the lamp to the boiling point. 2. A bent glass tube, B, to which a wooden scale is fixed. 3. A cylindrical glass vessel, O, filled with mercury and the wine to be tested. 4. A cylinder of sheet brass, in the upper part of which a thermometer, T, is fixed. The glass vessel, O, is filled with mercury to the mark, *a*, and then completely filled with the liquid to be tested. The boiling-vessel is now affixed, the brass cylinder drawn over the mercury tube, and the thermometer inserted. Heat is applied, and the water raised to the boiling-point; the steam ascends into the brass cylinder, and heats the wine and mercury to the boiling-point of water. The wine expands, and is partly vaporised, forcing the mercury up the arm, B, which has been previously graduated by experiments with fluids of known alcoholic contents; the mercury of course rises the higher the more alcohol there is contained in the wine. The variable constituents of the wine, the extractive matter, &c., do not influence the result. The carbonic acid must have been removed previously by filtering the wine through freshly-burnt lime. Equally good, if not better, results are, however, to be obtained by the distillation test, effected by distilling 10 c.c. of the wine, and adding to the distillate sufficient water to make a total of 10 c.c., the specific weight of the fluid giving the alcoholic contents of the wine. The alcoholometer most generally employed is the *Ebullioscope* of Tabarié, Fig. 229. With the barometer at 760 m.m. water boils at + 100°, and alcohol at + 78·3° C. The nearer therefore the boiling-point of the fluid tested approaches 78·3°, the greater the alcoholic contents. The wine is poured into the vessel, C, and the cover, E H, replaced. The fluid is heated by means of the lamp, L, and the steam ascends round the thermometer, *t t′*, the height of the mercury of which when the fluid boils varies inversely as the alcoholic contents of the wines tested. The vessel, M M′, is filled with cold water to hasten the condensation of the vapours. If the boiling point of pure water be taken at 99·4° C., the following boiling-points show the quantity of alcohol contained:—

96·4° C.	3 per cent. alcohol.	91·1° C.	9 per cent. alcohol.
95·3 ,,	4 ,, ,,	90·2 ,,	10 ,, ,,
94·3 ,,	5 ,, ,,	89·7 ,,	11 ,, ,,
93·5 ,,	6 ,, ,,	89·3 ,,	12 ,, ,,
92·7 ,,	7 ,, ,,	88·8 ,,	13 ,, ,,
91·9 ,,	8 ,, ,,	88·4 ,,	14 ,, ,,

Red French wines contain 9 to 14 percentage by volume of alcohol; Burgundy, 9, 10, and 11 per cent.; Bordeaux, 10, 11, and 12 per cent. Other French wines contain 8 to 10 per cent.; the wines of the Palatinate, 7 to 9·5 per cent.; Hungarian wines, 9 to 11 per cent. Champagne contains 9 to 12 per cent.; Xeres, 17 per cent.; Madeira, 17 to 23·7 per cent. Acids exist in all wines, and are generally carbonic, succinic, tartaric, malic, and acetic acids; these acids are found partly free, partly combined as salts; tartaric acid, for instance, as *cremor tartari*, bitartrate of potash, and other acid tartrates. **Fauré** found an essential gum, which he termed œnanthin, and which with glycerine—first shown by Pasteur in 1859 to be a normal constituent of wine—helps to give a certain consistency to the wine. Pohl found (1863) in Austrian wines 2·6 per cent. glycerine. As wine ages the glycerine disappears. The colouring matter of wine is of interest in the

FIG. 228.

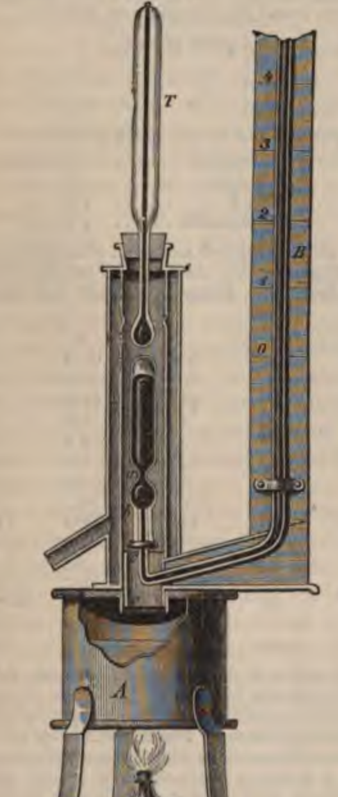
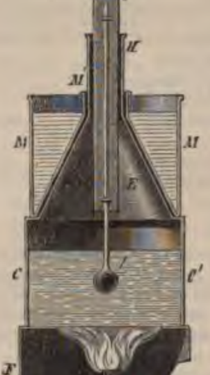


FIG. 229.



case of red wines only, as the yellow-brown colour of some wines is undoubtedly due to oxidised extractive matter. The colouring matter of red wines has received from Mulder and Maumené the name of œnocyan, while it is commonly termed *wine-blue*; it is a blue substance similar to litmus, possessing the property of turning red in the presence of acids. It is insoluble in water, alcohol, ether, olive oil, and oil of turpentine; but soluble in alcohol containing small quantities of tartaric or acetic acid. With a trace of acetic acid the solution is practically blue, turning red upon the addition of more acid; neutralised with alkalies the solution remains blue. On the evaporation of a wine to dryness the extractive matter remains, consisting of a mixture of non-volatile acids, the salts of organic and inorganic acids, with œnanthin, colouring matter, sugar, protein substances, and extractive matter, the nature of which is unknown. The quantity of extractive matter differs greatly, varying with the kind of wine and the degree of fermentation of the sugar. Fresenius found in Rhine wines a maximum of 10·6, and a minimum of 4·2 per cent. of extractives; Fischern, in the wines of the Palatinate, 10·7 to 1·9 per cent.; in Bohemian wines, 2·26; in Austrian, 2·64; in Hungarian, 2·62 per cent. The mineral constituents of wines exist in but small quantities—as an average in old Madeira to 0·25 per cent.; in old Rhine wines, 0·12 per cent.; and in old ports, 0·235 per cent. Van Gockom, Veltmann, and Mösmann found in 1000 parts of wine:—

Madeira	2·55 parts of ash.
Teneriffe	2·91 " "
Rhine wine	1·93 " "
Port	2·35 " "

Pohl estimated the following number of parts of ash in 100 parts of wine:—

Bohemian	1·97 parts.	Slavonian . ..	1·91 parts.
Croatian	1·68 "	Styrian..	1·63 "
Craniola	1·81 "	Tyrol	1·84 "
Lower Austrian ..	2·00 "	Hungarian	1·80 "

The ash contains potash, lime, magnesia, soda, sulphuric acid, and phosphoric acid.

The "Handwörterbuch der Reinen und Angewandten Chemie" (B. ix., Seite 676), gives the following analyses of wine-ash, the first four being by Crasso, and the fifth by Boussingault:—

	1.	2.	3.	4.	5.
Ash (per cent)	0·26	0·34	0·41	0·29	0·18
Potash	65·5	63·9	71·3	62·0	45·0
Soda	0·3	0·4	1·2	2·6	—
Lime	5·2	3·4	3·4	5·1	4·9
Magnesia	3·3	4·7	4·0	4·0	9·2
Oxide of iron	0.7	0·4	0·1	0·4	—
Oxide of manganese	0·8	0·7	0·1	0·3	—
Phosphoric acid	15·4	16·6	14·1	17·0	22·1
Sulphuric acid	5·2	5·5	3·6	4·9	5·1
Silica	2·0	2·1	1·2	2·2	0·3
Chloride of potassium	1·5	2·1	1·0	1·5	—
Carbonic acid	—	—	—	—	13·3
	100·0	100·0	100·0	100·0	100·0

The bouquet of wines or their peculiar odour is due to œnanthic ether mixed with the alcohol. According to C. Neubauer ("Chemie des Weines;" Wiesbaden, 1870, Seite 97), this œnanthic ether is a combination of various substances, of which caprylic and caproic acid ethers are the most important, and is a product of the fermentation of the must. During the fermentation of the sugar there are formed, besides ordinary alcohol, propylic and butylic alcohols, and succinic acid as a constant product, while in the juice of the grape there occur tartaric, malic, and racemic acids; these with acetic, propionic, and butyric acids, and the aldehydes of these acids, together with the oil of the seed of the grape (oleic and palmitic acids), cannot but greatly influence the bouquet of the wine, which of course will vary according to the proportion of these constituents.

Maladies of Wines. Wines are subject to various causes of deterioration, termed maladies, distempers, or diseases. That most commonly occurring is *ropiness or viscidity*, the cause of which was for a long time unknown. Francois showed that it was due to the decomposition of the glucose into azotised matter and mannite, and at the same time indicated the proper remedy, the addition of tannic acid. He employs 15 grms. of tannin to 230 litres of wine. This is well mixed with the wine, which is allowed to stand for a few days. At the end of this time the tannin will have separated the azotised matter, and the wine may be bottled off.

The *souring* of wine is due to the conversion of the alcohol into acetic acid, caused, according to Pasteur, by the formation of the vinegar plant or *Mycoderma aceti*, which he found in all sour wines. This disease is very common, and may result from too small a proportion of alcohol, too high a temperature of the cellars, or exposure to the atmosphere. The wine, if too far soured, is fit only for making vinegar; but slight cases can be remedied by an addition of sugar. The formation of vinegar may be somewhat delayed by impregnating the wine with sulphurous acid. In some cases the acetic acid may, by the addition of tartaric acid, be removed as acetic ether; but the acetic acid can never be neutralised with alkalies, as the salts formed are very easily soluble.

The *bittering* of wine, or its acquirement of a bitter flavour, is due to another cause, the formation of a bitter substance, which developes as the wine ages, or at too high a temperature. Maumené suggests as a remedy the addition of slaked lime in the proportion of 0·25 to 0·50 grm. per litre. Bittering is due also to the formation of brown aldehyde resin. *Mould* in wines appears as a white vegetable (fungus) film covering the surface, and arises from an insufficiency of alcohol; consequently weak wines are more subject to this malady. The film of mould should be removed and the wine used as soon as possible, for wine affected with this disease soon turns sour. The *decaying* of a wine is due to the dissipation of the alcohol and the decomposition of the acids of the wine; the wine obtains an astringent taste, and a dim, thick colour, finally turning sour. The bitartrate of potash is converted into carbonate of potash, affecting the colouring matter and tannic acid, which pass over into humus substances. At the commencement of this decomposition a remedy may be found in the addition of a small quantity of sulphuric ether. *Caskiness*, or the taste of the cask, due to an essential oil formed in casks that have long stood empty, is best removed by the addition to the wine of a small quantity of olive oil and agitation; the olive oil absorbs the essential oil, and brings it to the surface of the wine, whence the oily matter may be skimmed, or the wine may be filtered through freshly burnt charcoal. All casks and vessels that have stood long empty should be well steamed before use.

Ageing and Conservation of Wines. The Pasteuring, a term which usage has substituted for pasteurisation, or the conservation and artificial ageing of wines, according to Pasteur's method, is a great improvement in the general treatment of wines to ensure their keeping. It consists essentially in heating the wine to 60° C., and for this purpose the apparatus designed by Rossignol is best suited. A metal cask, T, Fig. 230, contains at the bottom a copper vessel, C, with a trumpet-shaped cover extending in the open tube, *c*, above the top of the vessel, T. *t* is a thermometer. Water is poured into the vessel, C, until the tube, *c*, is three parts full. The wine is placed in the metal cask, T, and by means of the tap, *r*, and the tube, *f*, run off into the cask, F, when sufficiently heated. The water in the copper vessel, C, is employed to prevent the direct heating by the flame of the vessel containing the wine, and the consequent burning of any insoluble matter settling to the bottom of the vessel. Fig. 231 shows in detail the manner of fastening the vessels together. A copper ring, *a*, encircles the vessel, T, and beds with the walls of this vessel into the india-rubber band, *d*, into which it is pressed by the tightening of the bolts, *e*, binding the ring of angle-iron and lower iron ring, *b*, together,. The joint is thus rendered water-tight. The vessel, T, is not quite filled with wine to allow for expansion under heat; by this means the wine is exposed to a known quantity of air. Wine should not be artificially aged in contact with air, as Pasteur has proved that such processes deteriorate the colour and the flavour of the wine; and in ordinary cases, where part of the process of ageing consists in heating the wines for a short time in an open vessel with a full exposure to air, the wine acquires a peculiar boiled flavour, *goût de cuit*, easily recognisable by the connoisseur. By Pasteur's method, however, neither the flavour nor colour of the wine is deteriorated; indeed, the latter is improved by the expulsion of the carbonic acid.

FIG. 230.

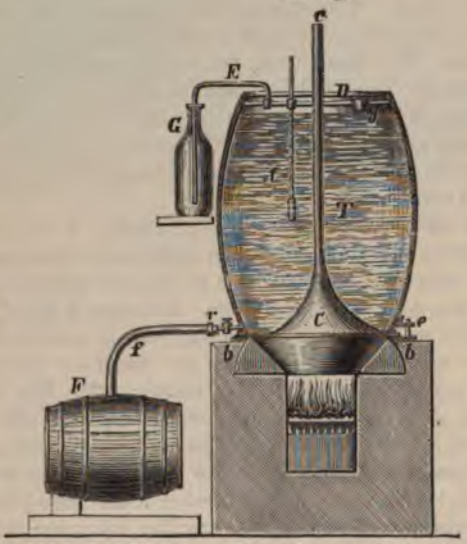
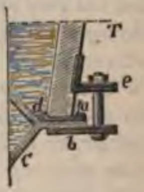


FIG. 231.



Pasteur has shown that most of the diseases of wine, acetification, ropiness, bitterness, and decay or decomposition, are due to the growth of different ferments, consisting of minute vegetable cells always existing in wines, and becoming active and destructive under certain conditions, such as a change of temperature and oxidation. He recommends ("Comptes Rendus," May 1st, 29th; August 14th, 1865), that these plants of fungi should be *killed*, as the best means of ensuring the keeping of the wine, and the particular *modus operandi* selected is essentially the following, differing considerably from the foregoing method. The bottles are quite filled, the wine touching the cork, which is inserted with such a degree of firmness that the wine in expanding may force the cork out a little, but not so much as to admit air into the bottle. The bottles are then placed in a chamber heated to 45° to 100°, where they remain for an hour or two, after which they are removed, set aside to cool, and the cork driven in. By this means the life or active principle of the fungi is destroyed, while the wine acquires an increased bouquet, is of a more beautiful colour, and, in fact, is to a considerable extent aged. Both new and old wines can be thus treated.

earing or Fining the Wine. Most wines are self-clearing, the ferment settling to the bottom of the cask, and leaving the wine clear and pure. This applies chiefly to dry wines which have less sugar than sweet wines. The sweet wines are generally more thickly fluid on account of the quantity of sugar they contain, and consequently more frequently need clearing. Fining, as it is sometimes called, or clearing, consists in adding to the muddy wine some albuminous or similar substance that will mix with the suspended matter and carry it to the bottom or bring it to the surface of the wine. The substances most generally employed are white of egg, ox-blood, and milk, or mixtures of these substances. Liming, or the addition of gypsum, is for the purpose of heightening the colour, chiefly of red wines; further, it converts the soluble potash salts of the wine into insoluble lime-salts and sulphate of potash.

The Residue or Waste of Wine-making. The waste of wine-making consists of the stems, husks, and seeds of the grapes, as well as of the fermentary sediment and tartar. Both descriptions of waste find numerous applications. The lees left from the pressing of the wine contain a not unimportant quantity of must, which (1) is employed in preparing an inferior wine. 2. In the making of an inferior brandy. 3. In the preparation of verdigris (see p. 58). 4. In vinegar making, and for promoting the formation of vinegar from saccharine or alcoholic fluids. 5. In wine-making countries the lees are much employed as fodder for horses, mules, and sheep. While (6) the residue of the after-pressing or final pressing is used as manure. 7. The grape seed yields an oil in quantities of 10 to 11 per cent.; or (8) tannic acid in large quantities. The oil can be extracted by pressure or by treatment with benzole, or with sulphide of carbon. The tannin obtained can be employed for the preservation of hides, &c. 9. Potash is prepared from the calcined lees. 10. The stalks and seeds when calcined are employed in the preparation of a black colouring material (vine black). 11. The ferment and stalks are in some wine-producing countries, besides being employed in the preparation of tartar and potash, also used in the distillation of a peculiarly rich brandy, in which an oil is found possessing highly the flavour of cognac, and known in commerce as wine oil, cognac oil, *huile de marc*. 12. Crude tartar is found with tartrate of lime, colouring matter, and yeast, forming a more or less thick crust on the walls of the wine cask or in the crust deposited in the wine, but not firmly attached to the vessel, and is the chief source of the pharmaceutical bitartrate of potash ($C_4H_5KO_6$), and tartaric acid.

Effervescing Wines. Effervescing wines have been known for many centuries. Some of Rembrandt's paintings exhibit among the accessories, a champagne glass with effervescing wine. And from Virgil—

"*Ille impiger hausit,*
Spumantem pateram—"

it would appear that this description of wine was known to the Romans. In 1870, there were in Germany fifty producers of effervescing wines, with a production of 2¼ to 3½ millions of bottles, 1¼ millions of which were exported. In France the production amounts yearly to 16 to 18 millions of bottles.

All wines are capable of being produced as effervescing wines if bottled before the fermentation is over. By bottling at this period the carbonic acid is retained in the wine, and when the bottle is opened the disengagement of this gas causes the appearance of effervescence. In this country the effervescing wine most generally known is champagne; but Hocks, Moselles, and even red wines are very admirable when thus treated. If the wines contain much sugar, the fermentation is arrested in the bottle before all the sugar is consumed, producing a sweet effervescing wine. On the other hand, if the sugar is all exhausted in producing the carbonic acid, the result is a dry effervescing wine. These wines are very agreeable to the palate, and may be supposed to assist the digestion of the food with which they are taken; but when new, they are dangerous as being likely to communicate their state of change to the contents of the stomach, interfering seriously with digestion, and producing what is well known as "acidity." Dry effervescing wines are less likely to disagree than sweet wines of this class containing much sugar and fermentable matter. The connoisseur places great reliance in his judgment of a champagne upon the loudness, or rather sharpness, of the report when the cork is drawn, and upon the "bead" or bubble formed on the side of the glass by the carbonic acid gas. These effects are not proportionate, for while a loud report results from an extended fermentation, a good bead may be obtained with a very weak fermentation. The gas in a bottle of champagne exerts a pressure of some five atmospheres, and it will at once be evident that if the bottle be made a little smaller, reducing the space between the cork and the wine only one-twentieth, a considerable increase in loudness of the report will ensue.

The process of manufacturing effervescing wines is in general the following:—The best grapes are used for this purpose; for champagne, the black grape, called by the French *noirien*, is employed. The juice is expressed from the grape as soon after gathering as possible, in order to prevent the colouring matter of the skin affecting the wine; while the fruit is pressed as quickly and as lightly as possible. The juice from the second and third pressings is reserved for inferior, or red-tinted effervescing wines. The expressed juice is immediately poured into tuns or vats, where it is left to stand for twenty-four to thirty-six hours. In this time any earthy matter or vegetable impurities will have settled, and the juice is ready to be transferred to the fermenting vats, where it remains for about fifteen days. It is then put into casks, which are securely bunged; sometimes brandy is added in the proportion of one bottle to one hundred bottles of juice or must. Towards the end of December, the wine is fined with isinglass, and a second time in the ensuing February. About the beginning of April the clear wine is fit for bottling. It now contains, if a good wine, 16 to 18 grms. of sugar, 11 to 12 per cent. of the volume of alcohol per bottle, and an equivalent to 3 to 5 grms. of sulphuric acid in free acids.

Great care is necessary in the manufacture of champagne bottles; they must be free from flaws, and made of pure materials. Generally each bottle is from 850 to 900 grms. in weight, and equal in thickness throughout. Formerly the flawed bottles amounted to 15 to 25 per cent., but recent improvements in manufacture have reduced the percentage to 10. Before the wine is introduced, the bottle is rinsed with a liqueur of white sugar-candy 150 kilos., wine 125 litres, cognac 10 litres, the liqueur being allowed to remain in the bottle: according to F. Mohr the cane sugar of the liqueur becomes converted into grape sugar in the champagne. It is doubtful whether glycerine might not be advantageously substituted for a portion of the sugar of the liqueur. The liqueur employed varies with the flavour of the wine: port, Madeira, essence of muscatels, cherry water, &c., are used, but rarely unmixed with some other favourite solution of the manufacturer, as, for instance, water 60 litres, saturated solution of alum 20 litres, tartaric acid solution 40 litres, tannin solution 80 litres. About 2 litres of this mixture would in practice be added to a butt of wine. The bottles are filled by women, the proportion of liqueur introduced being about 15 to 16 per cent. of the wine. A space of about 2 to 3 inches is left between the wine and the cork, which, after being thoroughly moistened, is next inserted by a machine. The bottle is then passed to a man, termed in the French establishments the *maillocher*, who drives the cork home with a mallet. Another process, now generally effected by the aid of a machine, is the "wiring," or securing the cork with wire or string. The bottles are now conveyed to the cellar, where they are laid in horizontal racks against the wall. In about eight or ten days a deposit, termed "griffe," is formed, and shows that the time has arrived for the wine to be transferred to the cellar, where it is to remain until sold to the merchant. The deposit is allowed to form during the summer, and in the ensuing winter means are taken for its removal. The bottles are well shaken, and placed with their mouths downwards, to cause the deposit to settle on the cork. The cork being removed, the sediment falls out, when more liqueur is added, and the bottle re-corked and again wired. The bottle is now laid upon its side at an angle of about 20°, and in about eight to ten days the inclination is gradually increased until the vertical position is attained, when, by a dexterous movement of the cork, the gas is permitted to force out the remaining sediment. This process is repeated as many times as may be necessary, until the wine is perfectly clear. Wine thus prepared, generally known as sparkling wine, *vin mousseux*, is ready for the consumer at the end of 18 to 30 months, the time varying with the temperature of the season. One of the greatest causes of loss is the bursting of the bottles, sometimes as much as 30 per cent. of the wine being wasted. This in some measure accounts for the dearness of these wines.

By the analysis of several sparkling wines (1867 and 1870) the following results were obtained:—

	1.	2.	3.	4.	5.	6.
	Per mille.	Per mille.	Per mille.	Per mille.	Per mille.	Per mille.
Free acid	5·300	5·900	7·600	7·800	6·200	5·600
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Alcohol	8·400	9·500	8·700	8·400	9·800	8·400
Sugar	8·200	4·300	7·900	9·100	7·500	5·400
Extractive matter	11·600	7·500	10·300	12·000	11·600	15·200
Specific gravity	1·036	1·029	1·039	1·046	1·039	1·041

1. From Chalons. 3 and 4. From Wirtzburg. 2. From the same place, but intended for export to India; 3 being the manufacture of J. Oppman, and 4 of Silligmüller, both well-known German firms. 5. From Sutaine and Co., of Rheims. 6. From a well-known Rhenish firm, glycerine being substituted for a portion of the sugar.

The Improving of the Wine Must. The worth or character of a wine is determined by its aroma and the amount of alcohol and free acid contained—decreasing with an increase of the latter, and increasing with increase of the former. The proportion between the chief constituents of the grape-juice, sugar, acid, and water, is nearly equal in all good wines, and this proportion is never accidental, but always belongs to a good wine. The grapes not fitted for making good wines are treated in two ways: either the expressed juice is allowed to ferment as it is, in which case an inferior wine is obtained; or, by the study of chemical analyses of good wines, the incomplete constituents are supplied, and others injurious to the wine removed, to make the must of that quality which will yield a good wine. The following are the best methods of improving the must:—

1. The addition of sugar to wine poor in this constituent, and the neutralisation of an excess of acid by means of pulverised marble (Chaptal's method).
2. The addition of sugar and water to must poor in sugar and rich in acid (Gall's method.)
3. Repeatedly fermenting the husks with sugar-water (Petiot's method.)
4. Removing the water by means of freezing, or by treatment with gypsum.
5. Removing the acid by means of a chemical reaction.
6. Addition of alcohol to poor wines.
7. Treating the prepared wine with glycerine (Scheele's method).

The addition of sugar to must poor in this constituent is the oldest method of improvement, and appears to have been known to the Greeks and Romans. At that time cane sugar was unknown, honey being used for sweetening purposes, and which, being added to the wine, gave it a peculiar flavour, and rendering it thick. In years when honey was scarce, we are informed that the wine was inferior. Chaptal, in 1800, wrote a work on the cultivation of the grape, in which he gives a recipe for adding sugar to an inferior must, to render the wine equal to that of better years, the acid being neutralized with pieces of marble. In Burgundys, Chaptal's method is not much required to be used, as these wines rarely contain more than 6 parts per 1000 of free acid. The amount of pulverised marble (carbonate of lime) required to neutralise 60 parts of free acid is, as a rule, 50 parts; and the amount of sugar to be added, when the acid is in excess, is 100 parts for each 50 parts of alcohol required after fermentation, it being found that 15 per cent. of sugar in the must produces 7·5 per cent. of alcohol in the prepared wine. Thus should it be desired to heighten the alcoholic contents from 7·5 to 10 per cent., to every 1000 kilos. of must are added 50 kilos. of sugar.

The cause generally of the poorness of the must in sugar is a wet or cloudy season, during which there has been but little warmth from the sun to ripen the grapes. Most German wines show, besides a lack of sugar, a superabundance of acid, malic and tartaric acids; and while the addition of a sugar solution increases the alcoholic contents, it does not remove these acids, which impart a flavour to the wine and lessen its worth. The addition of a saccharine solution does not, as might be expected, enfeeble the bouquet of the wine, if pure starch sugar, containing no dextrine, be employed. The use of impure starch sugar causes a quantity of unfermented matter to remain in the wine, imparting to it a tendency to decay. Gall's method is found to be economical, as a flavouring material can be added to very inferior must. According to Gall a normal must should consist of—

Sugar	24·0 per cent.
Free acid	0·6 ,,
Water	75·4 ,,
	100·0 ,,

1000 kilos. of such a must contain, therefore 240 kilos. of sugar, 6 kilos. of free acid, and 75·4 litres of water. If, by analysis, the must to be improved yields only 16·7 per cent. sugar and 0·8 per cent. acid, there are to be added—

153 kilos. of sugar, and
180 ,, or litres of water,

by which addition 1333 kilos. of normal must are obtained, corresponding to an increase in quantity of 33 per cent; while in some years, when the acid contents are as much as 12 to 14 per cent., the increase in quantity rises to 100 to 115 per cent., but seldom more.

Petiot based his method on the fact that, according to the usual process of preparing the must, the colouring and bouquet constituents remaining in the marc are sufficient to give the flavour and odour of wine to a lixivium of sugar-water. This method may, therefore, very justly be considered as yielding a wine without the aid of grape-juice. To the marc left after the expressure of the grape-juice cold water is added, equal in quantity to the must removed: in this water the marc is allowed to macerate for 2 to 3 days. The water takes up the various soluble constituents of the marc; after the time specified the liquor is removed, and the amount of sugar and acid it contains ascertained. There is usually only 2 to 3 per cent. of sugar, consequently an addition of 17 to 18 per cent. must be made; and if there should be too little acid, tartaric acid must be added to approximate the acid contents of a normal must. The artificial must, as it may be considered, is then put into the fermenting vat, while the marc is again treated in a similar manner, a longer immersion being this time required. The resulting wines are darker in colour than wines prepared from the natural must, in consequence of a larger proportion of tannin. The flavouring of these wines is a matter of experience, and does not fall under any chemical consideration.

Freezing is employed in the improvement of wine, for the purpose of reducing the aqueous contents. According to the experiments of Vergnette-Lamotte and Boussingault, the effect of cold upon wine is of a very complicated nature. By cooling the wine at a temperature of 0·6° there first occurs the precipitation of those substances that are insoluble at this temperature. These consist of cream of tartar; colouring matter, and nitrogenous substances, and a fluid possessing the property of becoming solid at 6°. When these substances are removed the wine becomes more ardent, richer in alcohol, and its peculiar merit is that it is not liable to after-fermentation, and can be kept in vats and half-empty casks. The removal of the acid from wine is effected best by means of carbonate of lime (pulverised marble, chalk), sugar of lime, or neutral tartrate of potash. An addition of carbonate of lime to the must, or to the wine, is not detrimental, in so far that the wine retains none, or a very small quantity, of the lime-salt. Carbonate of lime will not be of service in the case of so-called acid fermentation, as acetate of lime will then be formed, and the wine is no longer worthy the name. Liebig recommends the use of neutral tartrate of potash for this purpose, as bitartrate of potash is formed, which settles as an insoluble salt to the sides of the vessel or bottle. The use of this neutralising agent has the merit, moreover, of not injuring the flavour and odour of the wine. Sugar of lime can be employed in the case of wines not containing acetic acid. To prepare the sugar of lime, slaked lime is diluted with ten times the quantity of water, to form a thin cream. This cream is thinned with sufficient water to obtain a milk of lime, in which sugar-candy is dissolved. The solution is left to stand, and the clear supernatant liquor—a solution of sugar of lime—decanted to mix with the wine as required. When the wine is treated with the sugar of lime solution, the lime forms with the acid of the wine an insoluble salt, which is precipitated, while the sugar remains in the wine.

Another addition to wine, hardly bearing upon its improvement, but effected as a means for its preservation during removal or exportation, is that known in France as the *vinage*, a certain quantity of brandy being mixed with the prepared wine. When the wine is to be exported from France, the law permits the addition of 5 litres of brandy to each hectolitre of wine, provided the alcoholic contents after the addition do not exceed 21 per cent. But experiments have proved that the wine delivered to private consumers does not on the average contain more than 10 to 11 per cent. of alcohol, while the wine delivered to retail firms averages 16 to 17, and to wholesale firms 22 to 24 per cent. To prevent this fraudulent proceeding, the operation of vinage is permitted only in the Departments of the Pyrénées Orientales, Aude, Hérault, Garde Bouches du Rhone, and Var, immediately under the inspection of the Commissioners appointed to this duty. In 1865, Scheele introduced his method of improving wine by the addition of glycerine, the addition being made after the first fermentation has subsided. The limits of the addition lie between 1 to 3 litres of glycerine to 1 hectolitre of wine. But the expense will not permit of extended operations.

BEER BREWING.

Beer. Beer is a well-known liquor obtained from germinated grain—chiefly barley and wheat, sometimes from rice, maize, potatoes, and starch sugar—and hops, by means of a yeast fermentation, but without distillation of any kind. It contains the constituents of the grain employed, which constituents by decomposition form dextrose, dextrine, and albuminous substances, alcohol, carbonic acid, small quantities of succinic acid and glycerine, organic matter, with phosphates of the alkalies and alkaline earths, besides the constituents of the hops.

In Bavaria, the *Schenk*, or *pot* beer, is brewed in the winter, and the *Lager*, or *store* beer, in the summer. The winter beer is brewed during October to April, when the highest range of the thermometer is 12° to 13°. A part of the beer by a short storing is set aside for winter consumption, while the remainder is used during the summer months.

1 volume of malt gives on an average 2·5 to 2·6 volumes of winter beer.
1 „ „ „ 2·0 to 2·1 „ summer beer.

In some of the North German States, potato-sugar and syrup are much employed in brewing, sometimes supplying a third part of the malt. But generally 1 cwt. of the malt gives—

300 quarts light beer.
200 „ double beer.
180 „ Bavarian or bock beer.

Materials of Beer Brewing. The materials of beer brewing are:—1. Grain, or amylaceous substances. 2. Hops. 3. A ferment. 4. Water.

The Grain.—The grain selected for this purpose is generally barley, as containing the proportion of sugar and starch best adapted to form alcohol. Many substitutes have been suggested, but with inferior success. In Bavaria, the large *double* barley (*Hordeum distichon*), is preferred. According to Lermer, 100 parts of dried barley contain:—

Starch	68·43
Protein substances	16·25
Dextrine	6·63
Fat	3·08
Cellulose	7·10
Ash and other constituents ..	3·51

The ash of barley contains in 100 parts:—

Potash	17
Phosphoric acid	30
Silicic acid	33
Magnesia	7
Lime	3

with other constituents. Potatoes, rice, maize, glycerine, and potato- or starch-sugar, are employed in some modern breweries.

Hops. The hop (*Humulus lupulus*), is a diæcious plant of the natural order o Urticaceæ, the female flowers of which; or catkins, are used for flavouring beer. The catkins, or strobils, are composed of a number of bracts or scales, which are green, afterwards changing to a pale yellow. At the base of each flower is seated the pistil containing the seed, while surrounding the pistil are a number of little grains, embedded in a yellow powder, the farina, containing the active property o the hop, essentially lupuline, the grains being termed lupulinic grain. This yellow pulverulent substance contains an essential oil, tannic acid, and mineral constituents. The essential oil, the flavouring principle of the hops, is found in air-dried hops, to the amount of 0·8 per cent.; it is yellow-coloured, with an acrid taste, without narcotic effect, of a sp. gr. = 0·908, turning litmus paper red. It requires more than 600 times its weight of water to effect a solution. It is free from sulphur, and belongs to the group of essential oils characterised by the formula, C_5H_8, and can become oxidised under contact with the air into valerianic acid ($C_5H_{10}O_2$), thi oxidation being the cause of the peculiar cheesy odour of old hops; it is a mixture of a hydrocarbon, C_5H_8, isomeric with the oils of turpentine and rosemary, with an oil containing oxygen, $C_{10}H_{18}O$, having the property of oxidation alluded to Tannic acid is found in the several kinds of hops, in quantities varying from 2 to 5 per cent., and is an important constituent, as it precipitates the albuminous matter of the barley, and serves to clear the liquor. It gives with the per-salts of iron a green precipitate; treated with acids and synaptase, does not separate into gallic acid and sugar; and by dry distillation does not give any pyrogallic acid. The *hop resin* is the important constituent of the hops, and contains the bitter principle or lupuline. It is difficultly soluble in water, especially in pure water, and when the lupuline or essential oil is absent. But water containing tannic acid, gums, and sugar dissolves a considerable quantity of the resin, especially when the essential oil is present. It is intensely bitter in taste, and becomes foliated when exposed to the atmosphere. Hop resin and the essential oil are not identical; the former is soluble in ether, the latter is not. In the course of long exposure it becomes insoluble. The gum and extractive colouring matter are of little use. The mineral constituents of hops dried at 100° are:—in ash, 9 to 10 per cent.; 15 per cent. of phosphoric acid; 17 per cent. potash, &c.

Quality of the Hops. The quality of the beer is almost proportionate to the quality of the hops. A rich soil is required for the growth of the hop-plant, well exposed to the influence of the sun's rays, and protected from easterly winds, which are highly detrimental. The hops must on no account be gathered until the seed is perfectly ripe, as it is only then that the bitter quality is fully developed. The ripeness of the hops can be ascertained by rubbing them between the fingers; if an oily matter remains, with a strong odour, they are fit for gathering. When gathered, the next most important operation is the drying, which is effected in kilns or stoves, at a temperature of 40°, with a good ventilation. When sufficiently dried, the small stem attached to the flower snaps readily. The temperature must be carefully regulated; not permitted to range so high as to run the risk of burning the hops, nor allowed to fall so low that the hops may afterwards become mouldy from under-drying. When dried the hops are carefully packed, the finer kinds being put into canvas pockets, and the inferior into hop-bags of a coarser texture. The bags are then subjected to slight pressure in a hydraulic or screw press, to render them more impervious to air. To preserve the hops they are sometimes sulphured, that is, subjected to the action of vapours of burning sulphur, 1 to 2 lbs. of sulphur being employed to 1 cwt. of hops. Old hops are sometimes treated in this manner, to impart the colour and appearance of freshly-dried hops, but the fraud can be detected by the odour. The best method of testing for sulphur in hops is as follows:—A sample of the hops is placed in a sulphuretted hydrogen apparatus, with some zinc and hydrochloric acid; the disengaged gas is passed through a solution of acetate of lead. If the hops contain sulphurous acid, sulphuretted hydrogen will be disengaged—

$$(SO_2 + 2H_2 = SH_2 + 2H_2O),$$

and black sulphide of lead thrown down from the lead solution. Better still is to receive the disengaged gas in a solution of nitroprusside of sodium, to which a few drops of potash-ley have been added; the slightest trace of sulphuretted hydrogen imparts a beautiful purple-red colour to the solution.

Substitutes for Hops. Other substances have been used as substitutes for hops, as the bark of some species of the pine, quassia, walnut leaf, wormwood, bitter clover, extract of aloes, &c.; recently picric acid has been employed. Although all these substances impart a bitter taste to beer, they are inferior to hops. They contain the same constituents, namely, tannic acid, a resin, a bitter extractive, and an essential oil.

Water. Water is employed for steeping the barley for the purpose of inducing germination. Brewers are careful as to the usual distinction of hard and soft waters. Soft water contains fewer mineral constituents. Rain, like distilled water, is a very soft water, containing traces only of organic matter, nitrates and carbonate of ammonia. Spring and well water are in most cases hard waters, while river water is often soft. Soft water, or nearly so, is best adapted for brewing. River water is preferred for malting. According to Mulder, in water containing lime an insoluble phosphate is deposited, while in the course of time lactic acid is formed. The water employed is usually purified by filtration through sand, gravel, and charcoal.

The Ferment. The yeast of former operations is generally employed in fermenting the beer-worts. The preparation of the yeast, and the *rationale* of the process of fermentation, given in a previous section of this work, should be consulted.

The Processes of Beer Brewing. The brewing of beer may be considered to consist of the following operations:—

1. The malting.
2. The mashing.
3. The fermentation of the beer-worts.
4. The fining, ripening, and preservation of the beer.

The Malting. 1. Malting is the process during which the grain—barley—is germinated, by means of steeping in water until it swells and becomes soft. The non-germinated grain possesses only in a very small degree the property of changing its starch into sugar (dextrose): this property is very fully developed during the germination, so much so that it would be an easy matter to distinguish between the germinated and non-germinated seed by the degree of this property alone. As has been already stated, barley is the grain preferred, on account of its forming sugar in larger quantities than any other kind of grain. The germination of the seed takes place in three well-marked periods. In the first, the seed is enveloped in an outer organ, which becomes exhausted and withered. In the second, the growth of the germ is shown by the swelling at the end by which it was attached to the stalk; and in the third period, the little plumule or *acrospire*, which would form the stem of the new plant, is put forth. The germinating seed is similar to an egg, with its white, yolk, and embyro; the shell corresponds with the outer or hard coating of the seed; the white and yoke of the egg appear as the albumen, or meal of the grain; while the embyro of the egg has its analogue in the germ of the grain. A remarkable change takes place during germination; the glutinous constituent has passed from the body of the grain to the *radicula*, or rootlet, which has grown to nearly the length of the grain, while about one-half of the starch has been converted into sugar. This conversion is the aim of the malting, as by its means the sugar can be readily dissolved. The grain is supposed to have been sufficiently treated when the *plumula*, or acrospire, has attained a length equal to two-thirds of the entire length of the grain. The operation of germination is the same with all kinds of grain employed in brewing. The conditions of success are—the saturation of the grain with moisture, and a temperature of not higher than 40° nor lower than 4°, with access of air and exclusion of light.

a. The softening or soaking of the grain is accomplished in large cisterns of wood, sandstone, or cement, half-filled with water. The grain is poured into the water, and after the lapse of an hour or so, sinks to the bottom of the tank, only the inferior and diseased seed remaining on the surface, to be removed with wooden shovels, and thrown aside for use as fodder for horses, cattle, &c. The steep water receives the soluble constituents of the husk of the seed, and becomes of a brown colour and peculiar flavour, with a decided inclination to lactic, butyric, and succinic acid fermentation. The duration of the softening varies according to the age of the grain, the temperature of the water, &c. A young fresh grain requires 48 to 72 hours' soaking, while an older grain, containing more gluten, is not thoroughly softened under 6 to 7 days. Grains of equal age and constitution must be soaked together, to obtain an equally softened product. After sufficient soaking the grain is allowed to drain for 8 to 10 hours, then taken out and thrown into heaps on the floor of the malt-house. The sufficiency of the soaking is ascertained—1. By pressing the grain between the finger and thumb-nail, when, if sufficiently moistened, the germ or embyro will be projected. 2. The husk is easily destroyed by pressure between the fingers. 3. When crushed with a piece of wood the grain yields a floury mass. The grain when softened has a peculiar aroma, resembling that of apples. The quantity of water usually absorbed by the barley amounts to 40 to 50 per cent. of its weight, while the grain correspondingly increases in volume 18 to 24 per cent. During this absorption the grain loses 1·04 to 2 per cent. of its own weight in solid matter. Lermer states, that in fresh steep water he has found succinic acid in the proportion of 30 grms. to 1 bushel of grain soaked.

b. *The Germination of the Softened Grain.*—As soon as the grain is thoroughly saturated with moisture, the conversion of the starch into sugar commences. When germination has proceeded far enough it must be stopped, as about this time the formation of sugar has reached a maximum. The softened barley is, as before stated, transferred to the floor of the malting-room, where it is "couched," or placed in a layer 4 to 5 inches in thickness. Here the germination proceeds till the plumules have attained the desired length. The temperature rises some 6° to 10°, on account of the heat developed during germination, and consequently much of the moisture is dissipated. The chief art of the maltster consists in stopping the germination at that point when the plumules and roots commence to draw upon the constituents of the grain. The duration of the germination varies, during the warmer months of the year, from 7 to 10 days, while towards autumn the process will not be completed under 10 to 16 days, but the average duration is 8 days. The grain during the germination loses about 2 per cent. of its weight, probably by the oxidation of the carbon to carbonic acid by the oxygen of the air.

c. The Drying of the Germinated Grain.—The grain is now removed to the drying floor (*welkboden*), where it is exposed to the air in layers 3 to 5 centims. in depth, and turned about with rakes 6 to 7 times daily. When the malt becomes dry it is cleared from the rootlets, some of which drop off by themselves, while others have to be removed by winnowing. Malt must be dried for the making of most kinds of beer, and has to undergo a roasting process before quite fitted for use. This drying or roasting is effected in a malt kiln or cylinder heated by flues to the boiling-point of water. During the roasting the malt acquires a darker colour, due to the conversion of the remainder of the starch into sugar. The equality of the temperature is of the utmost importance, so that one part of the malt may not be more strongly heated than another. Before the malt is submitted to this operation, however, it is first heated to 30° or 40°. By this means some of the starch is converted into gluten, and forms a coating to the grain impervious to water, the malt being in this stage known as "bright" malt from its smooth glossy appearance.

The malt kilns consist essentially of the drying plates upon which the malt is laid, and the heating flues. The plates used to be of stone or sheet-iron, but modern brewers employ wire-wove frames, placed one above the other, so that the hot air from the flues beneath may ascend through the interstices. The flues are generally of sheet-iron for the better conduction of heat to the surrounding atmosphere. Coke is used as fuel on account of the absence of smoke; as with coal or wood in the event of a leakage in the flues considerable damage would be done to the malt.

The malt is not all dried at the same degree (50° to 100° C.), but is distinguished as pale, amber, brown, or black malt, according to the degree of heat to which it has been exposed. Pale malt results from heating to 33° to 38°; amber, from a temperature of 49° to 52°; and brown from the rather high temperature of 65·5° to 76·5°. Black malt, commonly called patent malt, is prepared by roasting in cylinders, like coffee cylinders, at a temperature of 163° to 220°. These darker malts are used in England for colouring porters and stouts.

100 parts of barley give 92 parts of air-dried malt. The loss of 8 parts may be thus accounted for:—

In the steep-water	1·5
During malting	3·0
During germination	3·0
Other losses	0·5
Total loss	8·0

The moisture in air-dried malt amounts to 12 to 15·2 per cent., which is expelled during the kiln drying. According to C. John (1869) 100 parts of dried barley give—

	I.	II.
Malt	83·09	85·88
Plumules	3·56	3·09
Radicules (rootlets)	4·99	4·65
Fermentary products	8·36	6·38
	100·00	100·00

The change undergone during the drying or roasting of the malt is shown in the following table, the result of Oudeman's analyses:—

	Air-dried Malt.	Kiln-dried Malt.	Strongly dried Malt.
Products of roasting	0·0	7·8	14·0
Dextrine	8·0	6·6	10·2
Starch	58·1	58·6	47·6
Sugar	0·5	0·7	0·9
Cellulose	14·4	10·8	11·5
Albuminous matter	13·6	10·4	10·5
Fat	2·2	2·4	2·6
Ash	3·2	2·7	2·7

The amount of sugar is undoubtedly increased during the process; and the dextrine appears to increase with decrease of starch, and *vice versâ*. The conversion of starch into dextrine and sugar is effected, as far as is known, by the agency of diastase. Dubrunfaut has only lately (1868) shown that malt presents another substance similar in its effect to diastase, and which he termed *maltin*. This principle is found to be much more active than diastase, so that with the same quantity of maltin which a known quantity of malt contains, ten times as much beer can be obtained as when diastase only is employed. Dubrunfaut has also found a second but less active substance. Its behaviour with respect to the decomposition of starch is similar to that of diastase; malt contains 1½ per cent., while only 1 per cent. of maltin is found. The treatment with alcohol necessary to obtain diastase destroys the maltin. Dubrunfaut believes diastase to be only a less active modification of these new substances.

Preparation of the Wort. 2. Under this head is included the preparation from malt of the wort—a saccharine fluid containing dextrine—and the flavouring with hops. The general method of preparation is in three operations:—

a. The bruising of the malt.
b. The mashing.
c. The boiling and flavouring of the wort with hops.

The Bruising of the Malt. *a.* Beer-wort, or the wort, as it is generally termed, is obtained by means of the extraction of the bruised malt with water. To the end that all the active principles may be extracted from the malt, it must be bruised or ground to a fine meal. The obtaining of a clear liquor after the extraction is effected by means of filtration. The grinding is ordinarily performed in a malt mill, a machine with rollers being preferred as affording a more equable product.

Mashing. *b.* The mashing is a most important operation, on success in which depends many of the good qualities of the beer. It is during this operation that not only the sugar and dextrine already existing in the malt are set free, but also the unconverted starch, by the aid of diastase, the water, and a favourable temperature, suffer conversion into sugar and dextrine. Lermer found in the best cases of mashing that only half the starch was converted into a corresponding quantity of sugar. The operation is very variously performed, but generally may be considered as effected by either of two methods:—

a. The Infusion Method, according to which the mash is prepared at a certain degree of heat, but never attains the boiling-point. The crushed malt is thrown into hot water (*first cast*) in the mash tun, and when the mash has reached a certain saccharine condition, a further addition of water is made (*second and third cast*). The infusion method is much employed in North Germany, France, England, Austria, and Bavaria.

b. The Decoction Method.—After the infusion has been made the mash is brought to the boiling-point, and

- α. A portion of the water evaporated to form a thick mass (*thick mash boiling*). At a subsequent stage, only a portion of the mash having been thus treated, the remainder of the mash is added, and
- β. The whole of the mash is heated to the boiling-point (*clear mash boiling*). During the clear mash boiling the hops are added.

The mashing vessels are either round tubs or wooden cisterns with a double bottom, the upper being perforated, and about an inch above the true bottom. Between the bottoms is a tap through which the wort is drawn off. In large breweries these bottoms are of metal instead of wood. The hot water is supplied from the bottom and not from the top of the vessel. Under the mashing vessel is situated a large reservoir, either of stone, cement, wood, or masonry, and destined to receive the fluid run off from the mash. The continuous stirring of the contents of the mash-tun or tub is effected either by hand or machinery driven by water or steam power.

Decoction Method. The general description of the mashing process having been given, we now pass on to the particular method of preparing the wort by decoction. The infusion takes place in the mash-tun, in which the required quantity of water is placed, and the malt to be mashed shaken in. The quantity of water employed in making the infusion is generally in the proportion of 202 volumes of water to 100 volumes of malt, both at the ordinary temperature. After the bruised malt has been well stirred in the water, the whole is allowed to stand for 6 to 8 hours. During this time the necessary quantity of water is heated to the boiling-point in the copper. The quantity of water used to prepare an estimated quantity of beer is termed the "cast," and the quantity of malt the "yield." In Bavaria the quantity of beer prepared from a defined quantity of malt is as follows:—

100 volumes of malt yield { 202·3 volumes of Schenk beer.
{ 173·4 ,, ,, Lager beer.

In order to produce this quantity of beer an equivalent quantity of water must of course be employed, so that in a Bavarian brewery to 100 volumes of malt there are taken of water—

	Schenk beer.	Lager beer.
For infusion	202·3 vols.	202·3 vols.
For mashing	170·0 ,,	130·0 ,,
	372·3 vols.	332·3 vols.

These proportions vary according to the quality of the grain, the state of the weather, the length of time of keeping, &c.

The various modifications of the decoction method are:—1. The Bavarian or Munich method. 2. The Augsberg-Nuremberg, or Swabian method, sometimes termed "sediment brewing" (*satz brauen*).

Thick Mash Boiling. According to the Munich method (thick mash boiling) the cast of water is divided into three portions, two of which are poured into the mash-tun to form a paste with the bruised malt. After this mash has stood for two to four hours, the remaining third of the water, which during this time has been heated to the boiling-point in the copper, is added, the whole of the mash attaining thereby a temperature of 30° to 40°. Then follows the first thick mash boiling; for this purpose the brewer draws the mashed grain to one side of the tun, and removes a portion to the copper, where for schenk beer it is boiled for thirty minutes, and for summer beer for seventy-five minutes. The quantity of mash boiled at each operation is generally about half the cast. The boiling mass is returned to the mash tun. Then follows the *second* thick mash boiling, which for schenck beer last seventy-five minutes, and for summer beer an hour. By means of the first boiled mash the contents of the mash tun are raised to a temperature of 48° to 50°, and by the second addition to 60° to 62°. After the finishing of the second mashing the *clear mashing* begins, that is, the thinly fluid part of the mash is placed in the copper and boiled for about fifteen minutes, and is then returned to the mash tun. The temperature of the mash is now 72° to 75°, and is most suited for the formation of sugar. The mash remains in the covered tun 1½ to 2 hours. During this time, and as soon as the clear mash has been removed from the copper, the latter is re-filled with a sufficient quantity of water for the purposes of brewing small beer. When the sugar has been properly formed and dissolved in the wort the latter is removed from the mash tun to the fermenting vessels. The remaining mash is then treated with hot water to yield small beer, 1 bushel of malt yielding 35 to 50 quarts of this beer. The residue of the small beer is again treated with water, the resulting infusion being employed in vinegar-making. The residue from this process is used as fodder for cattle.

The thick mash boiling is by no means a rational method, as the separation of the mash and the several removals are unnecessary labour, and do not contribute so much to the complete extraction of the malt as is generally supposed; the high temperature renders a portion of the diastase ineffective, while much of the starch remains unconverted into dextrine and dextrose.

All who have tried to reduce the brewing process to simple methods based upon sound chemical and physical principles declaim against the process of thick mash boiling, stating—and with good sound reason proved by experiments—that the advantages of this method are absurdly overrated; and that in order to lessen the bad effects of this method as much as possible it should be replaced by a method of hot mashing, viz., at a temperature of from 60° to 65°.

Augsburg Method. Distinct from the foregoing mash methods is the so-called "sediment brewing" used in many Swabian and Franconian breweries. It essentially consists in treating the bruised malt with cold, and then with hot water to obtain a saccharine wort. The bruised malt is mixed with cold water in the mash tun in the proportion of 7 Bavarian bushels to 30 to 35 eimers (each = 68·41 litres of water. After standing for four hours, two-thirds of the fluid is drawn off. During this time a quantity of water (48 eimers to 7 bushels of bruised malt) is brought to the boiling-point in the copper; a portion of this water is now added to the contents of the mash tun, which thus attains a temperature of 50° to 52°, while the liquor or weak wort drawn off from the mash tun is poured along with the rest of the water in the copper. The liquor that has been drawn off contains albumen, diastase, dextrine, and dextrose. The mash is allowed to stand for a quarter of an hour in the tun, when the fluid is entirely drawn off, transferred to the copper, and heated to the boiling-point. This is termed the "first mash." While this is going on enough fluid will have drained from the malt in the mash tun to fill the space between the double bottoms of the tun; this fluid is at once removed to the cooling vessels. The fluid heated in the copper is now returned to the mash tun, the entire contents of which attain a temperature of 72° to 75°. This "second mash" is after an hour's interval followed by a "third mash." The wort is then run into the cooling vessels.

Infusion Method. The infusion method is distinguished from the decoction method by a slight difference in the procedure, the bruised malt being treated with water at a temperature of 70° to 75°, but without any portion of the mash being boiled. The method is that usually employed in this country, North America, France, Belgium, and North Germany.

The quantity of water intended to be used for the mashing process is, according to the initial temperature of the water the brewer has at hand, heated either wholly or only a portion in the copper, the temperature of this fluid being raised in winter to 75°, in summer to from 50° to 60°. The necessary quantity is first poured into the mash tun, the bruised malt being next added, and the mixture made up so as to form a moderately thin paste. Water is heated to the boiling-point in the copper in order to proceed further with the mashing process. As soon as a sufficient quantity of water boils it is—usually by means of properly constructed pipes—allowed to run into the mash tun, wherein it is considerably cooled owing to the colder water (liquor) present in that vessel; the increase of temperature of the contents of the tun to 75° (the most suitable for saccharification) is generally made in order to prevent the formation of starch paste, whereby the formation of diastase would be interfered with. Since the conversion of amylum (starch) into dextrine and dextrose proceeds gradually only, it is clear that the contents of the mash tun should be kept at the temperature suitable for that process; while, however, on the other hand, care has to be taken to prevent the mash becoming sour by the formation of lactic (probably also propionic) acid.

The progress of the formation of dextrine and dextrose is best ascertained by the help of an aqueous solution of iodine, or preferably of iodine dissolved in iodide of potassium, in the proportion of 0·1 grm. of iodine and 1·0 of iodide of potassium to 100 c.c. of water; this solution will at first give with a sample of the mash a dark blue colouration, next a wine red, and finally, when only dextrine and dextrose are present, no colouration at all. The addition of two to three drops of the clear wort to a small quantity of this iodine solution is sufficient for testing. When the mash has been kept for about one hour's time at the temperature most suitable for the saccharification, the wort is run either into a large reservoir, or into a vessel kept expressly for this purpose, or lastly, at once into the copper; and a fresh quantity of water is then poured into the tun, and the contents of the tun are allowed to remain for half to one hour at a temperature of 75°. It is as a matter of course quite evident that the infusion method may be varied as regards the quantity of water and repeated number of infusions; but in order to brew a beer of a certain and fixed brand it is requisite that the degree of concentration of the wort be always the same. For the purpose of ascertaining the degree of concentration, Balling's saccharometer is generally employed, which instrument when put into sugar solutions indicates the percentage of sugar they contain. Balling has shown that solutions of dry extract of malt have the same specific weight as cane sugar solutions of equal percentage. For use in a brewery the saccharometer need only be graduated for solutions varying between 20 to 30 per cent.

Extractives of the Wort. The quantity of extract which a wort should contain depends, of course, upon the quality of the beer which the brewer desires to make, and differs according to the nature of the beer, whether it shall be thick, heavy (rich in extract), or strong (of great alcoholic strength). The quantity of malt extract varies in different beers from 4 to 15 per cent., that of the alcohol from 2 to 8 per cent. 1 per cent. of sugar in the wort yields after fermentation 0·5 per cent. of alcohol. To produce a beer containing 5 per cent. of alcohol and 7 per cent. of malt extract, the wort should, before fermentation, mark the degree on the saccharometer corresponding to 17 per cent. A beer of 3·5 per cent. of alcohol and 5·5 per cent. of malt extract will have resulted from a wort containing 12·5 per cent. of sugar.

Boiling the Wort. *c.* The prepared but not yet boiled wort contains dextrose, dextrine, some unconverted starch, protein substances, extractive matter, and organic salts. The colour of the wort is a brown or yellow-brown, according to the variation of colour of the malt from which it has been obtained. The odour is agreeable and the taste sweet. The wort exhibits an acid reaction to test-paper, owing to the presence in that fluid of small quantities of free phosphoric, lactic, and probably other acids; but in case the wort has by accident become sour, or if wort is made purposely from already exhausted grain which has become sour, this reaction is far stronger, and may be ascertained by the odour, owing to the formation of volatile acids, among which butyric, and in the latter case, lactic and propionic acids are present in large quantity. The boiling of the wort aims at its concentration, and also at the extraction of the bitter principle of the hops; further also for the purpose of coagulating and precipitating a portion of the albuminous substances, by the aid of the tannic acid contained in the hops. This latter reaction renders the wort clear. In many breweries gypsum is added to the boiling wort to reduce the whole of the nitrogenous substances. The boiling is generally effected in copper cauldrons (technically, also simply, "the copper"), set in masonry over a fire-grate. The fire is very carefully disposed to prevent the burning of the wort, as the pans are exposed to the direct action of the flame. The manner of hopping (as it is termed), that is to say, the mode of adding the hops to thewort, varies in different breweries, and depends as regards quantity also upon the quality (strength) of the hops, the larger or smaller amount of extract contained or desired to be retained in the beer, and last, but not least, the mode of preservation and length of time it is intended to keep the beer.

Adding the Hops. To winter beer, which in Germany, as a rule, is consumed in four to six weeks after brewing, the old hops (viz. one year old), are added in the proportion of 2 to 3 pounds to a Bavarian bushel of malt (2·22 hectolitres). For summer beer, to be consumed in May and June, 4 to 5 lbs. of new hops are added to the bushel of dried malt; while for the beer for September and October consumption, 6 to 7 pounds of new hops are employed with each bushel of malt. Among the constituents of hops which are active in the process of brewing, we mention in the first place the bitter ingredient it contains (not correctly known, notwithstanding recent research) and which as well imparts to beer its bitter taste as its narcotic property; further, the tannic acid which combines during the boiling of the wort with a portion of such of its protein compounds as are not rendered insoluble by the boiling alone, and form together a precipitate, rendering the wort—previously turbid—quite clear, and also regulating the first and second (so called after) fermentation. The essential oil and resin met with in hops act to a certain extent as retarding the fermentation, and thus as preventatives of converting the wort into a sour liquid; as regards the inorganic constituents of hops they do not appear—at least cannot be directly proved—to be of much consequence. As regards the degree of concentration to be given to the wort by the process of boiling, it should be observed that the degree of concentration as ascertainable by the saccharometer should remain from 0·5 to 1 saccharometrical percentage under the degree of concentration which the wort should indicate at the beginning of the fermentation, because while cooling, the wort gains in concentration just the percentage alluded to. The separation of the coagulated albumen does not take place until the temperature of the wort has reached 90°; and the quantity separated is greater from wort prepared by the infusion method than from that prepared by the decoction method. As soon as it appears that in a sample of the boiling wort taken from the pan and poured into a large test-glass the suspended flocculent matter settles rapidly to the bottom of the glass, the boiling can be discontinued, the wort being then ready; but in the case of the infusion method, the boiling is continued for the purpose of further concentrating the liquor, and the boiling for this purpose may even last for from 5 to 8 hours. If the boiling only aims at the coagulation of the albuminous compounds, one hour's boiling in winter, and three-quarters of an hour in summer, is quite sufficient. As regards the hops, it is best to add them in a somewhat cut up state, and not before, by a good boiling of the wort, the greater part of the albuminous compounds have been, as far as possible, precipitated. In order to extract the hops, the wort is either passed through a basket filled with hops or through any suitably constructed perforated vessel retaining the hops, this vessel being placed in communication with the coolers; or the hops are boiled along with the wort; or again, several portions of the wort are boiled successively along with the same quantity of wort; and lastly, even with the weakest wort or after-run.

Cooling the wort. The cooling of the wort to the degree necessary for the commencement of the fermentation is effected in large wooden, stone, or iron cisterns. As at a temperature of 25° to 30° C. the wort has a great tendency to set up lactic acid fermentation, the cooling has to be very rapid in order that the temperature of the liquid may be soon much below 25° to 30°, and thus any danger of souring prevented.

The cooling of the wort is an operation which is performed in well constructed and in all directions well ventilated buildings, protected from rain, in which buildings the coolers are placed. Owing to improvements in the modes of cooling, it is now possible even to brew beer in localities (as for instance Montpellier and Marseilles, Barcelona, and Naples) where formerly, on account of the prevailing high temperature during the greater portion of the year, brewing could not take place at all; while also for the same reason in various countries (America, United States especially), excellent lager beer is brewed. The cooling vessels are generally only 6 to 8 inches deep, of wood, iron, or copper, and are placed in an airy situation near or immediately under the roof of the brewery. Metallic vessels are of course more effectual in cooling the wort in a short time than wooden ones; they are also more cleanly, and less liable to get out of order. In some breweries, where a constant stream of cold water is available, the coolers are placed therein; but this is of course a matter entirely depending on the locality of the brewery. Without doubt the surest means of cooling the wort rapidly is by employing ice, either in blocks in the wort or in pans placed in the cooling tuns. But for economic reasons this plan is not generally available. The temperature to which the wort is to be cooled is that best suited to fermentation, the next process to which the wort is subjected. The following are the temperatures at which fermentation most readily sets in, depending upon the temperature of the locality and upon the kind of fermentation:—

Temperature of the locality where the fermentation takes place.	Temperature of the wort.	
	In sedimentary fermentation.	In superficial fermentation.
6° to 7°	12°	15°
7° to 8°	11°	14°
8° to 9°	10°	13°
9° to 10°	9°	12°
10° to 12°	7° to 8°	12° to 11°

The concentration of the boiled and hopped wort is expressed in degrees per cent of the saccharometer.

According to J. Gschwändler's researches (1868), the undermentioned Bavarian beer worts had the following composition :—

	Decoction.	Bock.	Sedimentary Method.	Infusion.
Sugar	4·850	7·100	4·370	5·260
Dextrine	6·240	8·600	7·610	6·680
Nitrogenous substances	0·790	1·350	—	—
Other constituents	0·410	0·630	0·950	0·700
Specific weight	1·050	1·073	1·052	1·051
Extract (direct estimation)	11·870	17·050	11·980	11·940
,, (according to Balling)	12·290	17·680	12·930	12·640

While the wort remains in the cooler a yellow-grey or brown sediment is deposited, consisting of a compound of coagulated albumen with the tannic acid of the hops, and some starch similarly combined. This sediment during the first cooling is formed in quantities varying between 3 to 4 per cent. of the quantity of the cooled wort; the sediment when washed and dried amounts to 0·5 per cent. of the quantity of malt employed.

The Fermentation. III. *The Fermentation of the Beer Wort.*—The wort when cool is run into the fermenting tanks, where fermentation sets in either spontaneously, or is induced by the addition of yeast. The first kind—spontaneous fermentation—sets in as soon as the wort, having been cooled down to the temperature most suitable for fermentation, is left to itself, and this fermentation is induced by the sporules of yeast (ferment cells) always present in all fermenting localities, which meeting with the wort, find in that liquid the proper conditions suited for their growth. This kind of spontaneous fermentation is applied usefully in the brewing of the Belgian beers known as Faro and Lambick, which are rich in lactic acid. Usually, however, yeast is added to the wort, and there is avoided the dangerous first stage of spontaneous fermentation, for by the addition of the yeast a regular and rapid fermentation is set up, but yet so regulated that the yeast only gradually converts the dextrose into alcohol and carbonic acid.[*]

The higher the temperature of the wort and of the locality the smaller the quantity of yeast required. A yeast formed by a violent fermentation and at a high temperature, has more active qualities than yeast formed at a lower temperature and by a longer fermentation. The first spreads itself rapidly over the surface of the fluid, and is termed *superficial* yeast (*oberhefe*): while the second sinks to the bottom of the vessel, and there continues its action; this is termed—*sedimentary*, or *bottom* yeast (*unterhefe*). The fermentations resulting from these two yeasts are respectively termed superficial fermentation (*obergährung*), and sedimentary fermentation (*untergährung*). The latter fermentation is induced in worts that are intended to yield beers of great durability, such as the Bavarian beers. The superficial fermentation is induced in such beers as are intended to be soon drunk. Where fermentation is induced in a wort at a low temperature and with deposit only (bottom-yeast) the so-called surface fermentation—that is to say, a vinous fermentation whereby yeast is carried to the surface of the fermenting fluid—is employed chiefly for such kinds of worts as are intended to produce a beer which is not required to be kept for any length of time, but rapidly consumed after having been brewed. The wort is in this instance generally rich in sugar (glucose); and while only a portion of this sugar is converted into alcohol (sweet beer being formed), the formation of a small quantity of alcohol (the wort being only lightly hopped), contributes largely to the preservation of this kind of beer. Surface fermentation is also induced in such kinds of worts as are either very concentrated or contain substances which to some extent retard, or might even altogether impede, fermentation; as, for instance, the empyreumatic substances present in a very highly roasted malt or a large quantity of hops, these conditions obtaining in the brewing of porter, stout, and, as regards hops, the bitter ale. Worts of this description come comparatively very difficultly into fermentation. Fermentation, no matter whether surface or sedimentary (the yeast is in this case slowly deposited as a sediment on the bottom of the vessel), exhibits the three following phases, viz.:—

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[*] The results of the researches made by Von Lermer and Liebig (1870), are of great importance for a rational basis of the brewer's business. According to these *savants*, an addition of sugar to a solution of dextrine, to which previously beer-yeast has been added, causes a large quantity of the dextrine to be converted into alcohol and carbonic acid, just as if the dextrine were sugar.

1. The chief fermentation, beginning soon after the addition of the yeast, characterised by the decomposition of glucose, by the formation of new yeast, and by an increase of temperature.

2. The after-fermentation, during which decomposition of glucose continues slowly, while the formation of new yeast cells does not ensue so energetically as in the first phase, the suspended particles of yeast settling down, and the beer becoming clear.

3. The quiet or imperceptible fermentation taking place when the after-fermentation is finished is characterised by a further decomposition of glucose, while the formation of yeast is not perceptible to any extent.

Sedimentary Fermentation. Sedimentary fermentation is employed in the brewing of the Bavarian schenk and lager beers, taking place in large fermentation vats containing 1000 to 2000 litres of wort. Recently, upon the suggestion of G. Sedlmayer, these vessels have been constructed of glass. The addition of yeast may be effected in two different ways: yeast may be either added to the wort, or a small portion of the wort is first separately brought into a state of fermentation, and next added to the bulk of the liquid. In the first case, *dry yeasting*, as it is termed, the yeast is placed in a small tub and wort poured over it, and these substances having been well mixed, the whole of the contents of the vessel are thrown into the fermentation vats, and there worked about by the aid of a stirring pole. According to the second method, *wet yeasting or yeast carrying*, to 1000 maas* of wort, 6 to 8 maas of yeast are added and well mixed with about 3 eimers of wort, the mixture being allowed to stand for four to five hours. After fermentation has set in, the fermenting liquid is mixed with the wort in the fermentation tank. The yeast intended to be used for this purpose should be obtained from a former and normal fermentation; it should not be too old, and should possess a pure odour (not be foul), thick consistency, and be frothy.

After the wort has been mixed with the yeast the following phenomena are exhibited:—After ten to twelve hours the decomposition of the dextrose becomes apparent by the evolution of bubbles of carbonic acid gas, which forms a wreath of white froth at the edge of the vessel. In another twelve hours larger quantities of a more consistent froth are formed, causing the surface of the liquid to exhibit a very peculiar appearance, which might be compared to that of irregular masses of broken up rocks; at the same time a more vivid evolution of carbonic acid takes place and becomes perceptible by the smell. The German term for this phase of the fermentation, *Das Bier Steht im Kräusen*, can hardly be expressed in English, but the meaning is the fermentation is in full force; these phenomena to continue with a regularly proceeding fermentation in full activity for from two to four days, and then gradually subside, there remaining on the surface of the liquid a somewhat brown-coloured film of froth, much contracted, and chiefly consisting of the resinous and oily constituents of hops.

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* The Bavarian maas is equivalent to 1·25 English quarts.

The yeast formed is only to a very small extent present on the surface of the liquid, as in the case of sedimentary fermentation the carbonic acid evolved cannot carry the isolated yeast cells to the surface. The temperature of the fermenting liquid increases at the beginning of the fermentation, so that the liquid becomes several degrees warmer than the air of the locality where the fermenting vats are placed. By the fermentation the wort loses the greater portion of its dextrose, about half of which is evolved in the shape of carbonic acid, while the remainder is converted into alcohol; further, a portion of the albuminous substances dissolved in the wort is rendered insoluble and deposited in the shape of yeast. On being tested with the saccharometer the liquid—for reasons just explained—exhibits after fermentation a less degree of strength than before. The difference in percentage shown by the saccharometer before and after fermentation is in direct proportion to the quantity of dextrose decomposed, and provides a means of ascertaining the course of the progress of the fermentation. If this difference be made the numerator of a fraction, the denominator of which is the percentage indicated by the saccharometer before fermentation, the value of the fraction will increase proportionately with the completeness or efficacy of the fermentation; if, for instance, a wort before fermentation marks a saccharometrical percentage of 11·5, and afterwards gives 5 per cent.; the difference 6·5 divided by 11·5 gives the coefficient 0·565, that is, of 100 parts of malt extract 56·5 per cent. are decomposed during fermentation.

After-Fermentation in the Casks. After the chief fermentation is completed, which for summer or lager beer requires nine to ten days, and for winter or schenk beer seven to eight days, the young or *green* beer is put into barrels, after having become quite clear by the separation of the yeast. Before the beer is vatted the scum present on its surface is removed. The yeast, settling to the bottom of the vat in which the fermentation took place consists of three layers, the middle being the best yeast; the lowest, decomposed yeast and foreign matter, is mixed with the yeast of the upper layer, and if not otherwise saleable is sometimes employed in the distilleries of malt spirits. The middle layer serves for further fermenting operations. In breweries where pure water (the reader should bear in mind that Bavaria is alluded to) is not to be had, this yeast is occasionally obtained fresh from other breweries. It is usual to fill casks or vats with winter beer at once quite full; but as regards summer beer several brewings are mixed in smaller vats in order to obtain an uniformly coloured mixture. The barrels are usually coated with pitch on the inside, the aim being to prevent the beer soaking into the wood, and thus giving rise when the cask is emptied to the formation of acetic acid. For the after-fermentation the beer is placed in stone cellars, which should be as cold as possible, so as to cause the after-fermentation to proceed as slowly as possible, and thus admit of the beer being kept until the brewing season opens.

In all parts of Germany, but mostly so in Bavaria, great attention is paid to the construction of the cellars: often these cellars are excavated in rocks, and some times ice-pits are placed in the cellars to keep them very cool. The after-fermentation of the beer sets in when it is vatted, the moment of the beginning of this process partly depending upon the condition of the beer when vatted and partly upon the temperature of cellar. The after-fermentation, which becomes apparent by the appearance of a bright white-coloured foam at the bung-hole, may set in immediately after the vatting of the beer, or may only become apparent some eight days after. Should the beer happen not to exhibit any sign of incipient after-fermentation, green, young, or new beer is added for the purpose of inducing this process. When the after-fermentation is finished, the bungs of the casks or tuns are not tightly fastened, and the beer is left in this condition (in the cellars of course) during the summer months. About a fortnight before the beer in the casks is intended to be tapped, the bungs are tightly closed in order to cause as much carbonic acid to accumulate in the fluid as will occasion the beer to foam on being tapped; but if beer happens to be vatted in very green condition, the bung-hole should not remain closed for so long a period, because then so violent a fermentation may set in that, on tapping the cask, its contents become too much agitated, and thereby a very turbid (full of yeast) beer is served to the customers. Sometimes the addition of liqueur (a solution of white sugar) is resorted to for the purpose of setting up a strong fermentation in very old beer. According to J. Gschwändler (1868) beer obtained by the processes alluded to has the following composition:—

	Decoction.	Bock.	Sedimentary Method.	Infusion.
Alcohol	2·810	3·380	2·940	3·130
Sugar	1·580	2·320	1·460	1·330
Dextrine	4·610	6·910	4·770	4·800
Nitrogenous substances	0·380	0·740	—	—
Other constituents	0·380	0·400	0·890	0·550
Sp. gr. of solution of extract	1·022	1·042	1·028	1·026
Extract (direct estimation)	6·570	9·980	6·230	6·130
,, (according to Balling)	6·950	10·380	7·120	6·680

Surface Fermentation. Surface fermentation is that induced in the worts intended for the brewing of the bottled beers of North Germany, Bohemia, Alsace, England, and Belgium. Beer obtained by this process of fermentation is not so lasting as that prepared by the sedimentary fermentation process. This difference is due to the fact that the surface fermentation goes on at a higher temperature, proceeds more rapidly, while the elimination of the nitrogenous compounds is also less complete. The reason why this process is preferred to the sedimentary fermentation process is that brewing, by the application of the last process, is so greatly dependent upon a low temperature that this mode of brewing cannot be continued throughout the whole year; while as regards the other process it may be continuously carried on, and the stock of beer kept ready for use can thus be considerably decreased. Surface fermentation, however, is the only plan for preparing briskly foaming and strong beers. Porter, stout, and ale could be brewed as well by the sedimentary method—although in the English climate this process would be more difficult to conduct successfully—but the main reason why the surface fermentation is employed for English malt liquors is that this method—by a great saving of time—is cheaper. The phenomena of the surface fermentation are similar to those of the sedimentary, with the exception that the process is by far more violent, the froth surging more to the surface of the wort. The yeast is employed in the same manner. An ingenious contrivance is adopted in the London breweries for the purpose of carrying off the yeast from the beer after it has undergone the process of fermentation. The wort is placed in large hogsheads, or *rounds*, the tops of which are fitted with wooden troughs. Into these troughs the yeast runs as it rises, and is carried away. The beer now becomes clear, and is pumped into the stone vats.

Steam Brewing. The extensive application of steam to the manufacture of beet-root sugar and alcoholic spirits has given rise to many suggestions for the substitution of heating by steam for direct firing in brewing. The heating is effected by a system of tubes similar to that described in the preparation of beet-root sugar (see p. 377). In brewing, however, though much would be gained by uniformly heating the worts, and by reducing the chances of burning, there would not ensue any great economising of fuel; but much labour might be saved. Steam could not be employed directly without a series of tubes, as the condensation would cause a great dilution of the mash.

Constituents of Beer. The constituents of a normal beer prepared from malt and hops (not from substitutes) are:—Alcohol, carbonic acid, undecomposed dextrose, dextrine, constituents of the hops (oil and bitter substance, no tannic acid), protein substances, a small quantity of fat, some glycerine, and the inorganic matter of the barley and hops. The acid reaction which a normal beer exhibits after the carbonic acid has been expelled from it by boiling is due to succinic and lactic acids, with traces of acetic acid, and perhaps propionic acid. The sum of all the constituents of a beer after the abstraction of the water is termed the total contents; the sum of the non-volatile constituents, the extractive contents. Beer rich in malt extract is termed rich, fat, or full-bodied beer; and that which is poor in extract, but contains much alcohol, the wort having been rich in sugar which has all been converted, is termed a dry beer.

The proportion of alcohol in beer can be estimated by distillation and the testing of the distillate with an alcoholometer, or by means of an ebullioscope, or with the help of a vaporimeter (see Wine-testing, p. 394). The following table shows the average weight per cent. of the alcoholic contents of several beers:—

	Per cent.
Wirtzburg lager beer (1870)	4·0—4·3
,, schenk beer..	3·3—4·2
Stuttgardt lager beer (1865)..	4·1
Culmbach lager beer (1865)	4·5
Coburg lager beer	4·4
Munich lager beer	4·3—5·1
,, schenk beer	3·8—4·0
Bock (Munich, 1870)	4·3—4·8
Porter (Barclay, Perkins, and Co., London, 1862)	5·5—7·0
Strasburg beer (1870)	4·21
Vienna beer (1870)..	4·1
Riçe beer of the "Rhenish Brewery" in Mentz	3·6

The quantity of carbonic acid in beer varies between 0·1 to 0·2 per cent. According to C. Prandtl (1868) dextrose is found in beer in quantities varying from 0·2 to 1·9 per cent. The quantity of dextrine, according to Gschwändler's analyses, varies from 4·6 to 4·8 per cent. The proportion of sugar to dextrine is never constant. The occurrence of protein substances in beer has not been sufficiently investigated to warrant an exact conclusion. It may be said that on an average malt extract contains 7 per cent. protein substances, from which Mulder deduces that 1 litre of beer should contain 5·6 per cent. albuminous substances. A. Vogel (1859) found that 1 Bavarian maas (= 1·069 litres) of beer on an average contained 1 to 1·2 grms. nitrogen; and Feichtinger (1864) obtained from 1 Bavarian maas of several Munich beers between 0·467 and 1·248 grms. nitrogen. Succinic acid, acetic acid, and lactic acid occur in Belgian and Saxony beers in large quantities. Tannic acid occurs in Bavarian beers only in small quantity. The inorganic constituents of beer have received great attention. Martius obtained from 1000 parts of Bavarian lager beer 2·8 to 3·16 parts ash, containing one-third potash, one-third phosphoric acid, and one-third magnesia, lime, and silica. J. Gschwändler and C. Prandtl (1868) found an average extractive contents in 100 parts of—

	Parts.
Schenk beer (Munich)	5·5—6·0
Lager beer (Munich)	6·1
Schenk beer (Wirtzburg	4·6
Lager beer (Wirtzburg)	4·4
Bock (Munich)	8·6—9·8
Salvator (Munich)	9·0—9·4
Rhenish rice beer	7·3
Porter (Barclay, Perkins, and Co., London)	5·6—6·9
Scotch (Edinburgh)	10·0—11·0
Burton ale	14·0—19·29

100 parts of extractive matter contain, according to A. Vogel (1865) 3·2 to 3·5 parts of ash; 100 parts of ash contain 28 to 30 parts phosphoric acid. 1 litre of beer contains 0·57 to 0·93 grm. of phosphoric acid.

Lermer (1866) subjected several Munich beers to analysis with the following results:—

	1.	2.	3.	4.	5.	6.	7.
Sp. gr.	1·02467	1·0141	1·01288	1·0200	1·02678	1·03327	1·0170
	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.	per ct.
Extractive matter	7·73	4·93	4·37	4·55	8·50	9·63	5·92
Alcohol	5·08	3·88	3·51	4·41	5·23	4·49	3·00
Inorganic constituents	0·28	0·23	0·15	0·18	—	—	—
Nitrogen:—							
In 100 parts extract	11·15	8·71	12·19	8·85	—	6·99	—
„ 100 „ beer	0·87	0·43	0·53	0·39	—	0·67	—

1. Bock beer. 2. Summer beer. 3. White beer. 4. White Bock beer (superficially fermented, obtained by surface fermentation from malted wheat). 5. Another sample of Bock beer. 6. Salvator beer. 7. Winter beer.

The analysis of the ash of five of these beers gave:—

	1.	2.	3.	4.	5.
Potash	29·31	33·25	24·88	34·68	29·32
Soda	1·97	0·45	20·23	4·19	0·11
Chloride of sodium	4·61	6·00	6·56	5·06	6·00
Lime	2·34	2·98	2·58	3·14	6·21
Magnesia	11·87	8·43	0·34	7·77	7·75
Oxide of iron	1·01	0·11	0·47	0·52	0·84
Phosphoric acid	34·18	32·05	26·57	29·85	29·28
Sulphuric acid	1·29	2·71	6·05	5·16	4·84
Silicic acid	12·43	14·12	7·70	2·86	8·01
Sand	0·83	0·67	2·30	5·20	6·27
Carbon	0·49	0·81	0·40	0·65	0·28
	100·33	101·47	98·03	99·08	98·91

The high importance of beer, both as regards its value as nutriment as well as regards the enormous trade done in this article, has given rise to attempts to find proper and suitable means for testing that liquid in respect of its quality and purity.

Beer-Testing. The experiments proposed for ascertaining the strength as well as freedom from adulteration of beer, is termed beer-testing; it is desirable that these operations should be easily executed and yield sufficiently reliable results. The strength of a beer is judged according to the quantity of alcohol, extract, and carbonic acid it contains; it is evident, however, that an intimate knowledge of the real constituents of the extract, viz., the therein contained quantities of dextrine, hop constituents, the by-products of alcoholic fermentation, such as, for instance, succinic acid and glycerine, not to mention such substances as, for instance, glucose and glycerine purposely added to the wort, as substitutes for malt, largely influence the quality of any kind of beer, and therefore ought to be determined when any rigorously exact analysis of that liquid is wanted.

Beer-testing is effected partly by ascertaining certain physical qualities of the beer, partly by chemical means. To the former belong its flavour, odour, colour,* consistency, transparency, specific gravity, refractive power to light, &c. By chemical analysis we ascertain and determine the immediate constituents, viz., carbonic acid, alcohol, extractives, and water. The carbonic acid contained in the beer is first eliminated either by repeatedly pouring a quantity of beer from one tumbler or beaker-glass into another, care being taken to let the beer fall from some height, or the carbonic acid is removed by shaking the liquid up in a bottle and pouring it out of the same and into it again. The gas having been driven off, the specific gravity of the beer is taken by means of the hydrometer or saccharometer; the beer is next boiled down to half its original bulk; next there is added to it it as much water (best distilled) as is required to restore the liquid to its original bulk, and of this liquid the specific gravity is again determined; this will be found greater than that previously obtained. The difference between the two determinations gives the amount of alcohol contained in the beer.

Balling's Saccharometrical Beer-Test. Since by fermentation 100 parts of malt extract yield 50 parts alcohol, twice the quantity of alcohol found will indicate the quantity of malt extract necessary for its formation. This quantity of malt extract added to that still existing in the beer indicates the whole of the malt extract existing in the wort before fermentation.

The specific gravity of the beer-wort becomes lower by fermentation, partly because the specifically lighter alcohol is formed, partly by the loss of some of the extractive matter, and partly also by the loss of the substances taken up in the yeast. This decrease of the specific gravity, or *attenuation*, as it is termed, can be estimated either directly by weighing, or by means of the saccharometer. The degree marked by the saccharometer in a beer freed from carbonic acid we will call m; the malt-extract of the wort, p. Subtracting m from p, the difference $(p-m)$ gives the *apparent attenuation*, which is the greater the more thorough the fermentation. The quantity of alcohol in a beer varies in direct proportion with the apparent attenuation. The empirical alcohol factor, a, by which the apparent attenuation must be multiplied to obtain the alcoholic contents of the beer $=$ A in weight per cent. $[(p-m)\,a = \mathrm{A}]$ becomes the greater, the higher the original degree of concentration of the wort. For worts between 6 to 30 per cent. of extractive matter, this factor varies from 0·4079 to 0·4588. The alcohol factor can be found by the following equation, when the apparent attenuation $(p-m)$ and the alcoholic contents of the prepared wort (A) are known; then $a = \left(\frac{\mathrm{A}}{p-m}\right)$. With the help of the alcohol factor, a, the alcoholic contents in weight per cent. can be calculated. A quantity of beer being boiled to volatilise the alcohol, and the residue having been diluted with water to the original bulk or weight, if a weighed quantity were operated with, the specific gravity gives the quantity of extractive matter contained in the beer, which Balling terms n. The difference between the extractive matter contained in the wort (p) and that of the beer (n), or $(p-n)$, gives the *actual attenuation*, which, multiplied by the *alcohol factor for the actual attenuation* (b), likewise gives the quantity of alcohol contained in the beer expressed in percentage by weight. The alcohol factor for the actual attenuation is $b = \left(\frac{\mathrm{A}}{p-n}\right)$. Subtracting from the apparent attenuation $(p-m)$ the actual $(p-n)$, the difference (d) in the attenuations is obtained:—

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* Very recently, C. Leyser has invented a colorimeter with which, by means of a normal solution of iodine (12·7 grms. iodine to a litre) after having brought the beers to an equal colouration with water, he estimates the relative degree of the original colour. The invention is fully described in the "Jahresberichte der Chem. Technologie" for 1869 p. 467

$$d = (p-m)-(p-n)\text{; or } d = m-n.$$

d is known, when the extractive matter contained in the beer (n) and the saccharometrical percentage (m) of the beer free from carbonic acid are known; d is the greater the more alcohol the beer contains. The alcohol factor multiplied by the difference in attenuation gives the percentage (A) of alcohol, from which the *alcohol factor for the difference in attenuation* can be obtained by the following equation:—

$$c = \frac{\mathrm{A}}{(p-m)}$$

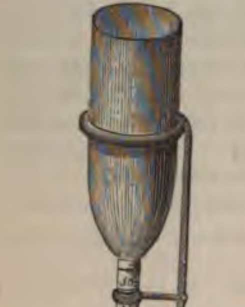
It averages 2·24. Finally, with the help of c the difference in attenuation of the alcoholic contents of a beer can be calculated approximatively, even when the quantity of extractive matter of malt contained in the wort is not known. The apparent divided by the actual attenuation gives a quotient (d), which is the ratio of the attenuations, $\mathrm{d} = \frac{p-m}{p-n}$, and can be calculated with the help of the alcohol factor for the apparent attenuation (a), and of the original extractive contents of the wort (p). First—(a) is obtained by the division of the alcohol factor for the actual attenuation by the corresponding attenuation quotient or ratio. Assuming the alcohol factor for the difference in attenuation to be $= 2·24$, and next doubling the approximative alcoholic contents thus obtained, we arrive at the quantity of the extractive matter of the wort from which the alcohol was formed. Adding to this the extract yet met with in the beer, the sum thus found expresses the approximate percentage of the extractive contents of the wort. When (p) has thus been approximately obtained, Balling's tables give the corresponding attenuation quotient q, reckoning all decimals above 0·5 as units, and neglecting those under 0·5. If only the original concentration of the wort (p) is to be calculated, the percentage of the alcohol of the beer may be obtained from the equation to the actual attenuation $\mathrm{A} = (p-n)\,b$. If the degree after fermentation is 9·75 (or 16·29 — 6·54), the saccharometrical percentage (see p. 363)

$$= \frac{9·75}{16·29} = 0·542.$$

Fuchs's Beer Test.

Hallimetrical Beer Test.—Fuchs's test, based upon the presumption that the beer has been brewed from malt and hops only, starts from the fact that 100 parts of water, independently of temperature, dissolve 36 parts of pure common salt (= 2·778 : 1), and that a fluid dissolves the less salt the greater the quantity of alcohol and extractive matter it contains. It is therefore possible to estimate by this means the quantity of water in a beer by determining the quantity of common salt which remains undissolved; this is done by means of the hallimeter, Fig. 232, an instrument consisting of two glass tubes, one very wide and cup-shaped, the other narrower and attached to the bottom of the former. The smaller tube is so graduated that the larger divisions correspond to a quantity of 5 grains of common salt, while the smaller divisions correspond to 1 grain of salt. In all hallimetrical experiments it is very essential that the pulverised common salt be always as much as possible of the same degree of fineness, while care has also to be taken that this substance be reduced to its smallest bulk when put into the tube by gentle taps, so as to expel air, and thus cause the salt to occupy exactly the space intended for it. It is therefore required to pass the pulverised salt through a wire-gauze sieve, after which the prepared salt is kept for use in a glass-stoppered bottle. The testing requires two experiments. By the first is estimated the amount of water together with the entire quantity of carbonic acid, alcohol, and extractive matter contained in the sample; while the second experiment gives the quantity of extractive matter, which when the carbonic acid is deducted from the total contents, yields the amount of alcohol contained in the beer. The alcohol is not anhydrous, but is mixed with a certain quantity of water. 1000 grains (62·5 grms.) of the beer to be tested are poured into a flask with 330 grains (20·46 grms.) of the common salt. The flask, lightly closed with a stopper or cork, is frequently agitated, and having been placed on a water-bath is heated to 38°. After six to ten minutes the flask is removed from the water-bath, the carbonic acid being expelled by gently blowing into the flask, which is next weighed; the loss of weight indicates the quantity of carbonic acid, which in good beer averages 1·5 grains. The mouth of the flask having been closed with the thumb is turned upside down in order thereby to collect any non-dissolved salt in the neck of the flask, and the salt along with the fluid transferred to the hallimeter, the non-dissolved salt settling down in the graduated tube, this movement being promoted by gently shaking the instrument. As soon as the volume of the undissolved salt ceases to increase, the number of grains is read off and deducted from 330, the difference being the number of grains dissolved from which the quantity of water present is calculated.

FIG. 232.



Example: 1000 grains (= 62·5 grms.) of beer dissolve 330 − 18 = 312 grains common salt; therefore these 1000 grains of beer contain 866·6 grains of water; for

$$36 : 100 = 312 : x,$$
$$\therefore \quad x = 866{\cdot}6$$

1000 − 866·6 = 133·4 grains indicate the total quantity of carbonic acid, extractive matter, and alcohol present in the beer. If the contents of the flask by heating have lost 1·5 grains in weight, the extractive matter and alcohol together amount to 131·9 grains. The second experiment is now made to estimate the amount of extractive matter. For this purpose 1000 grains (62·5 grms.) of beer are weighed off and poured into a flask, and boiled down to half the quantity, that is, 500 grains. Both the carbonic acid and the alcohol are driven off. 180 grains of common salt are now added, and the experiment proceeded with as before. Supposing $180 - 20 = 160$ grains of common salt to be dissolved, there will have remained 444·4 grains of water; for

$$18 : 50 = 160 : x$$
$$\therefore\ x = 444{\cdot}4,$$

which shows the quantity of the extractive matter to be 55·6 grains. If the preliminary estimation of the carbonic acid has been correct, the quantity of alcohol contained in the beer will be 76·3 grains, for $133{\cdot}4 - 55{\cdot}6 - 1{\cdot}5 = 76{\cdot}3$. This corresponds, according to a table published with each instrument, to 42·27 grains of absolute alcohol. The beer would, therefore, contain in 1000 parts:—

Carbonic acid	1·50
Free water	866·60
Combined water	34·03
Extractives	55·60
Alcohol	42·27
	1000·00

The hallimetrical assay of beer is entirely worthless when beer is made with the addition of glucose or glycerine.

By-products of the Brewing Process. Among the by-products of brewing the residue of the mash tuns is perhaps the most important. 100 parts of kiln-dried malt leave on an average 133 parts of residue, which being dried at the temperature to which the malt was subjected give 33 parts. It is used as fodder for cattle under the name of brewers' grains. This material yet contains, in addition to the husks and cellulose of the grain, undecomposed fatty matter and protein substances, upon which its value depends. Exhausted mashed grain from a Munich brewery used to prepare summer beer (by the thick mash method) had the following composition:—

	Wet Grains.	Air-dried.	Dried at 100°.
Water..	74·71	7·28	—
Ash	1·06	3·87	4·18
Cellulose	3·06	11·22	12·10
Fat	1·70	6·23	6·72
Nitrogenous nutritive matter.. ..	6·26	22·89	24·71
Non-nitrogenous nutritive matter	13·21	48·51	52·29
	100·00	100·00	100·00

The rootlets and plumules of the germinated malt present in the proportion of about 3 per cent. of the weight of the dried malt, form a very concentrated and rich fodder. According to the analyses of Scheven, Way, and Lermer (Hungarian barley), the following is the composition of that substance:—

	Scheven.	Way.	Lermer.
Water	7·2	3·7	10·72
Ash	6·8	5·1	6·91
Cellulose	17·0	18·5	—
Protein substances	45·3	48·9	32·40
Non-nitrogenous nutritive matter	23·6	23·8	49·77

The sediment of the cooling tuns (see p. 414), part of which is used as fodder and part in the preparation of brandy, amounts to about 3 per cent. of the wort. The after-washes are also used in malt spirit making, as well as in the preparation of vinegar. The thick mash processes yield an after wash containing from 4 to 8 per cent. extract, while by the infusion methods this amounts only to 2 to 3 per cent. Much of the yeast formed during brewing is employed in bread-making, as well as in the manufacture of vinegar and brandy

THE PREPARATION OR DISTILLATION OF SPIRITS

Alcohol. Since alcohol happens to be in almost all countries an article which in a nearly pure state (that is to say more or less diluted with water) is a fluid used as an article of consumption, and therefore very properly submitted to a more or less heavy duty or impost, the mode of manufacturing alcohol on the large scale, and the raw materials from which it is obtained, vary in different countries, and consequently these conditions very greatly influence the industry of alcohol production. When a fluid containing alcohol is distilled, alcohol and water are collected in the receiver, while the non-volatile constituents remain in the retort in a concentrated condition. The act of distillation of an alcoholic fluid is termed the *brennen*,* while the product of the operation is designated as brandy, a fluid which contains on an average from 40 to 50 per cent. of alcohol. A distillate which contains more alcohol than the quantity just alluded to is designated as spirits of wine, or simply spirit. Originally, that is to say when spirits (now some two and a half centuries ago) were first commenced to be made industrially on the large scale, it was only made for the purpose of being drunk, and the liquor prepared in the comparatively dilute state in which it is offered for sale for consumption. More recently (within the last forty or fifty years), the use of alcohol in various branches of industry (varnish-making, ether preparation, perfumery, preparation of cordials, liqueurs, &c.) is so great, that as a rule distillers at once prepare strong alcohol, which, if required for consumption as a beverage, is suitably diluted and sweetened if desired. Since the distillation of alcohol has been carried on on the large scale the apparatus have been very greatly improved; and those now in use in the best arranged distilleries are constructed upon scientific principles, while care is also taken that the surveillance on the part of the excise officers is rendered an easy task, and fraud almost impossible. The whole art of the production of alcohol—its ready preparation from grain (partly malted), from beet-roots, potatoes, refuse of saccharine liquors from sugar works, the proper utilisation of the residues of the distillation, either as food for cattle or otherwise—is now brought to a degree of perfection almost unequalled in any other branch of industry.

Alcohol and its Technically Important Properties. The formula of alcohol (as a chemically pure substance) is C_2H_6O, or $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$. It is a colourless, thin, very mobile fluid of 0·792 sp. gr., boiling at 78·3°, while water boils under the same atmospheric pressure at 100°; thus there is afforded a means of ascertaining by the boiling-point of an alcoholic fluid, the quantity of alcohol contained. Between 0° and 78·3° (its boiling-point), alcohol expands 0·0936 of its volume, while the coefficient of expansion of water between the same degrees is 0·0278. The expansion of alcohol is thus $3\frac{1}{3}$ times greater than that of water; and this fact is made available in alcoholometry. The tension of the vapour of alcohol at 78·3° is equal to an atmosphere, while water must be raised to a temperature of 100° to obtain the same pressure. Thus, the variation in height of a column of mercury subjected to the pressure of these vapours may be made a measure of the quantity of alcohol contained in a fluid. On this principle the vaporimeter (see p. 395) is constructed. Alcohol is readily inflammable, and burns with a pale blue flame without giving off soot. Its heat of combustion corresponds to 7183 units of heat. It eagerly absorbs water, and upon this property is based its use for the preservation of articles of food, cherries, and other fruit, and also anatomical preparations. It mixes with water in all proportions, whereby a decrease of bulk of the mixture and increase of specific gravity is observed—

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* There is no equivalent term for this word in English neither also in the French language; the real meaning is "the firing," in Dutch (*branden*); the term *Brennerei* (German), and *brandery* (Dutch), meaning "a distillery."

53·9 volumes of alcohol, with
49·8 ,, water, form a mixture not of
103·7, but of 100 volumes.

Alcohol is a solvent for resins (upon which property is based its application to the manufacture of varnishes, cements, and pharmaceutical preparations), and also a solvent of many essential oils. These solutions are employed either as perfumes, such as eau de Cologne, or as liqueurs, cordials, and aqua vitæ, or as spirits for burning in lamps, as, for instance, the mixture of oil of turpentine and alcohol, so-called fluid gas; alcohol also dissolves carbonic acid gas, a property made available in the making of effervescing wines.

By the influence of certain oxidising agents alcohol is converted first into aldehyde and next into acetic acid, as illustrated in the so-called quick vinegar-making process. Alcohol does not dissolve common salt, and upon this property Fuch's test (see p. 422) is based.

By the action of most of the stronger acids aided by heat alcohol is converted into what are termed ethers; as regards the action of sulphuric acid upon alcohol, it depends upon the relative quantities and degree of concentration of these liquids, whether sulphovinic acid, ether, or bicarburetted hydrogen gas, be formed. Hydrochloric acid forms with alcohol chlorine of ethyl or hydrochloric ether. Butyric and oxalic acids form ethers directly when heated along with alcohol; but most of the other organic acids require the addition and the aid of sulphuric or hydrochloric acid for this purpose. Alcohol is the intoxicating principle of all spirituous liquors.

Raw Materials of Spirit Manufacture. Alcohol is always the product of vinous fermentation. The manufacture of spirits therefore includes three principal operations:—

1. The preparation of a saccharine fluid.
2. The fermentation of this fluid.
3. Separation of the alcohol by distillation

All saccharine fluids, therefore, or those substances which yield alcohol by fermentation, can be employed in the manufacture of spirit; and all materials so employed contain already either completely formed alcohol, or cane sugar and dextrose, or finally substances which by the influence of diastase or dilute acids are converted into dextrose. Such substances are starch, inuline, lichenine, pectin compounds, and cellulose. The raw materials of spirit manufacture may be generally classed in the three following groups:—

1st Group.—Fluids in which the alcohol is already present, requiring only distillation to effect its separation. Such fluids are wine, beer, and cider.

2nd Group.—Substances either solid or liquid which contain sugar, which may be either cane sugar, or dextrose and levulose, or sugar of milk. In this group are included the beet-root, carrot, sugar-cane, maize stalk, the Chinese sugar-cane (*sorghum*), some kinds of fruit—viz., apples, cherries, figs, some berries (grapes, mountain ash berries, &c.), the melon and gourd, some fruits of the cactus tribe, the molasses of cane and of beet-root sugar manufacture, the marc of grapes and refuse grain of beer-making, honey, and milk.

3rd Group.—All substances which originally contain neither alcohol nor sugar, but the constituents of which may be converted into sugar and dextrose. Such are starch, inuline, lichenine, pectin compounds, and cellulose, chiefly found in—

a. Roots and bulbs: Potatoes, dahlia roots, &c.

b. Cereals: Rye, wheat, barley, oats, maize, and rice.

c. Leguminous and other seeds: Buck-wheat, millet, black or negro millet, peas, lentils, beans, vetch, chestnut, horse-chestnut, oak leaves, &c.

d. Substances containing cellulose: Sawdust, paper, straw, hay, leaves, osier, moss.

In the future a—

4th Group may perhaps be added, which will embrace all substances as probably may enter into the synthetic preparation of alcohol, and thus form what might be called a mineral spirit. Berthelot in 1855 proved that alcohol can be formed from olefiant gas and water ($C_2H_4 + H_2O = C_2H_6O$). Olefiant gas, when agitated for a length of time with concentrated sulphuric acid, gives rise to the formation of sulphovinic acid; and from this liquid after having been diluted with water a dilute alcohol can be distilled. This experiment has as yet only a scientific interest; the process has been tried on the large scale in France, but failed to be commercially available.

a. Preparation of a Vinous Mash.

Vinous Mash from Cereals. Grain brandy (corn brandy) may be prepared from either wheat, rye, or barley. Generally more than one kind of grain is used, because experience has proved that a larger quantity of alcohol is obtained when two kinds of grain—for instance, wheat and barley, rye and barley—are mixed. A mixture of rye with wheat or barley malt, or wheat with barley malt, is very generally used, at least abroad. To 1 part of malt from 2 to 3 parts of non-malted grain are usually taken. Either, as is done in England, wort is made, the grain being first malted, next mashed, and the wort drawn off, or the mixture of malted and unmalted grain is allowed to ferment together. The latter method is more usual in Germany, and will be that described in this work. In Russia and Sweden brandy is prepared without malting; by properly mashing rye meal a reaction ensues between its constituents, the effect of which is the same as if it had been acted upon by diastase of malt—

The preparation of a mash from grain may be considered as consisting of the following four operations:—

1. *The Bruising.*—The materials, malted as well as unmalted grain, are first bruised. As it is not essential in the manufacture of spirits that a clear wort should be prepared, the grain may be broken up very small, whereby the formation of sugar is rendered more complete. Green malt is now generally considered preferable by many distillers.

2. *The Mixing with Water.—Making of Mash.*—This operation is almost identical with that of the mashing of the brewer; the only distinction being that the distiller aims at the entire conversion of the starch into glucose, while the brewer does not require this as he also wants some dextrine. The complete saccharification, and next the complete conversion of the glucose into alcohol during fermentation, are possible only with a certain degree of dilution of the mash. The quantity of water to be mixed with the grain cannot be reduced too much, because that would involve a loss of spirits.

3. *The Cooling of the Mash.*—When the saccharification is complete, the mash should be rapidly brought to the temperature suitable for fermentation by being placed in cooling vessels, just as is done with the wort in brewing, by being placed in an apparatus termed a refrigerator, or by the application of ice or cold water. The temperature to which the mash has to be cooled varies according to the locality and the duration of

the fermentation, but it averages 23° C. When sufficiently cooled the liquid is placed in the fermenting vats.

4. *The Fermentation of the Mash.*—The fermentation vat is generally made of wood and sometimes of stone. The first possesses the property of retaining the heat for a longer time, and for the same reason large vessels are preferred. The capacity seldom exceeds 4000 litres. Either beer yeast in its fluid condition or dry yeast is used to set up fermentation. The latter is mixed with warm water before being added to the contents of the fermentation tanks. Of the fluid beer-yeast, there is usually taken to 1000 litres of mash 8 to 10 litres; while for 3000 litres of mash 15 to 20 litres of yeast are a sufficient quantity. Of the dry yeast, $\frac{1}{3}$ a kilo. is employed to 1000 litres of mash, or 1 kilo. of yeast to 3000 litres of mash. In large distilleries artificial yeast is sometimes employed, as beer yeast of the requisite quality cannot always be procured at a remunerative price. The mode of adding the yeast is the same as that employed in breweries. After standing 3 to 5 hours the temperature of the mash will have increased to 30° to 32°. Carbonic acid is then given off, and the heavier substances settle to the bottom of the tank. This continues for about four days, when the clear fluid may be considered ready for further operations.

Mash from Potatoes. Potatoes consist of about 28 per cent. of dry substances, 21 per cent. of which is starch, with 2·3 per cent. of albuminous matter, and 72 per cent. of water. The active principle under the influence of which the starch is converted into dextrose is diastase, but this substance is not found even in the germinated potato. It therefore becomes necessary, in order to convert the starch of the potatoes into dextrose, to add malt, or to treat the potatoes first with dilute sulphuric acid. Accordingly, the preparation of a mash from potatoes may be performed by either of these two operations. The former is that most generally employed. The preparation ordinarily includes the following operations:—1. *The washing and boiling of the potatoes.*—Before the potatoes can be boiled or steamed, they must be cleansed from the adhering earth. After the washing the potatoes are boiled without previous paring. Finally, they are steamed. 2. *The chopping of the boiled potatoes.*—As soon as the potatoes are boiled they are placed in a chopping machine, and cut into small pieces, care being taken to keep them hot by the aid of steam, so that the cut up mass admits of being readily mixed with hot water into a uniform mass, which is the best condition for the potato starch to be most readily converted into dextrose. In some cases the boiled potatoes are passed between two hollow cast-iron cylinders, the axles of which are so arranged and fitted in a frame-work as to admit of the cylinders being moved in an opposite direction, and thus capable of converting the boiled potatoes into a uniform mash. 3. *The mashing.*—After the addition of the grain or diastase-containing material, the mashing proceeds as in the case of malt. The grain or malt added is sometimes rye malt, sometimes barley malt, and generally a mixture of the two. Green malt has greater power of conversion than air-dried malt, ultimately producing a larger quantity of alcohol. The proportion of bruised malt to be employed varies in many instances; while in some cases only 2 to 3 per cent. of barley as malt is added to 100 parts of potatoes; in others as much as 10 per cent. is used. A medium quantity between these two extremes, or about 5 per cent., is perhaps that most in use. 100 parts of potatoes containing about 20 per cent. of starch yield on an average 17·3 parts of dry extractive matter in the mash wort, 5 parts of barley malt yielding 3 parts of dry malt extract; the yield of spirits has therefore to be calculated from these two substances. When a thick mash of potatoes is made a different proportion of the dry substances to the water to be added is obtained from that which obtains when malt or raw (unmalted) grain is made into a mash; these proportions are in the case of potatoes as 1 : 4·5, 1 : 4, even 1 : 3. It is clear that the large quantity of water contained in potatoes (viz., 72 to 75 per cent.) has to be taken into account.

The operation of cooling is performed as already described. While the mash is placed in the cooling vessels it undergoes changes which are partly favourable and partly unfavourable to the yield of alcohol. The increase of sugar is of course favourable; this increase can only be accounted for by the action of the protein compounds contained in the malt, whereby the dextrine is converted into dextrose. All albuminous substances possess the property of converting starch into dextrose; and this the more so if the albuminous substances are themselves already in a state of decomposition. Blood, brain, albumen of malted barley, saliva, meat in a state of incipient decay, are all capable of converting starch into dextrose. When Mulder suggests that the word diastase should be banished from science, and for it substituted that of starch converter, he is right in a scientific sense, because diastase does not exist as a chemical body by itself; but the word diastase may be conveniently used in technology for the purpose of indicating an albuminous body, which being itself in a state of decomposition, is capable of converting starch into dextrose. Another change of the mash consists in the formation of lactic acid, always readily formed from sugar under the influence of a peculiar ferment. The quantity of this acid is increased by slowly cooling to the suitable temperature for fermentation; it is therefore best to cool the mash as rapidly as possible. Recently, an aqueous solution of sulphurous acid is employed, some of this being added to the mash mixture, the effect being the prevention of the formation of lactic acid, and thus increased yield of alcohol.

Mash with Sulphuric Acid.

The Preparation of a Mash by means of Sulphuric Acid.—We have already seen that some dilute acids are as capable of converting starch into dextrose as the so-called diastase of malt: dilute sulphuric acid is usually applied for this purpose. Leplay first recommended this mode of preparing mash. The raw potatoes are first converted into a pulp, which is thrown into a large vessel containing water. The starch cells separate, some settling to the bottom of the vessel, others becoming mixed with the cellular tissue of the pulped potatoes. The brown-coloured supernatant fluid (wherein is also contained the albumen of the potatoes, which would, if left, interfere with the action of the sulphuric acid upon the starch) is first syphoned off. This liquid is given as drink to cattle, or is used for the purpose of moistening dry fodder. While this operation is in progress there is heated to the boiling-point in another vessel the required quantity of dilute sulphuric acid, the heating apparatus consisting generally of steam pipes. To every hectolitre of potatoes from 1·5 to 2 kilos. of strong sulphuric acid diluted with 3 to 4 litres of water is usually taken. The previously more or less washed green potato starch is gradually and by small quantities at a time added to this boiling fluid. The boiling is continued until the whole of the starch as well as all the dextrine are converted into glucose, the course of the progress of the conversion being ascertained by means of iodine water, while the insolubility of dextrine in alcohol affords a means of ascertaining whether the conversion of this substance is complete. A sample of the fluid when agitated with alcohol should exhibit no milky appearance. After about five hours' boiling the formation of sugar will be complete. The fluid is then first run into a vessel with double bottoms, one of which is perforated with small holes so as to admit of acting as a strainer to retain cellular tissue, &c., after which the fluid is run into another vessel, and while therein is neutralised by the addition of chalk. The gypsum having settled down, the fluid is again transferred to another vessel. The wash water of the sediment having been added, the liquids are ready to undergo fermentation.

4. *The Fermentation of the Potato Mash.*—The addition of yeast to the cooled mash in the fermenting vat takes place in the same manner as with malt. To 100 kilos. of mash are added 1 to 2 litres of beer yeast, or ¾ to 1 kilo. of dry yeast. The potato mash contains besides the husk of malt and grain some finely divided cellular tissue; these substances during fermentation are carried to the surface of the mash and form a scum, the appearance and behaviour of which gives an opportunity of judging the progress of the fermentation. The fermentation is said to be regular or irregular; the former begins some four to six hours after the yeast has been added, and proceeds in a regular manner, the end depending upon the quantity of yeast added and upon the temperature. The progress is quiet, not violent, the scum which appears on the surface sinking or being drawn down at one side of the vat and thrown up at the opposite side, while bubbles of air or gas appear and burst on the surface, much as bakers' dough heaves under the influence of the ferment. Irregular fermentation is so far opposed to the former that the surface of the mash is only partly covered with froth, which remains in one position, and does not move of itself. The result of such a fermentation is generally defective, the reason being the incomplete saccharification of the mash, the addition of too small a quantity of yeast, or finally working at too low a temperature. After about 60 to 70 hours with a regular fermentation, the mash is ready for distillation. Recently large quantities of spirits have been prepared from maize and also from rice.

Mash from Roots. By the use of those vegetables which contain alcohol-forming bodies, either in the shape of cane sugar or as dextrose, the mashing process is avoided, and the prepared fluid is immediately ready for fermentation as soon as the saccharine fluid has been completely squeezed out of the cells wherein it is contained in the vegetable. The great advantage of the preparation of spirits with the avoiding of the mashing process is too important to be overlooked, and it is therefore clear that every effort should be made to substitute for the starch-containing vegetable products those which contain sugar, the more so as it has been recently proved in England perfectly possible to arrange this industry in every way to the satisfaction of the excise authorities.

One of the most important of such roots is the sugar-beet so largely employed in the manufacture of beet-root sugar. Although it would appear to be a simple matter to extract the juice from the previously pulped juice, this is yet—notwithstanding even the large quantity of juice, viz., 96 per cent. of the weight—a difficult matter, because the remaining 4 per cent. of substance have all the properties of a sponge and tenaciously retain the juice; it is this spongy nature of the solid constituents of the root which prevents the conversion of the whole root into a sufficiently concentrated mash. If it were possible to set up fermentation in the thick pulp obtained from the roots 100 kilos. of the pulp would yield 6 litres of alcohol, a quantity sufficiently large to be remunerative even with a very low market price of spirits. Indeed it is maintained by the advocates of beet-root distilleries, that the distillation of spirit is a more profitable business than the manufacture of beet-root sugar. In Belgium and Germany, distilleries are frequently to be found attached to the beet-root sugar manufactories; and the combination of the industries possesses the advantage that, in a season when the proportion of sugar in the roots is too poor to yield much profit to the manufacturer as sugar, he may ferment the sugar-containing juice and obtain a fair yield of spirit. Beets to be available to the distiller may contain only 5 to 6 per cent. of sugar; but for the purposes of the manufacturer of sugar they must contain at least 8 to 9 per cent. The products of the first distillation of the fermented beet-roots contain, in addition to water, oils known as fusel oils, of very unpleasant taste and smell and of poisonous quality. These oils, however, disappear during rectification. The methods of obtaining the juice are the following:—

- α. By pulping and
    - a. Pressure, or
    - b. By treatment in a centrifugal machine.
- By maceration, or by the dialytical method.
    - a. The sliced roots being treated with cold or with hot water (Siemens' and Dubrunfaut's methods).
    - b. The sliced roots being treated with hot wash from former distillations.

γ. According to Leplay's method, somewhat modified by Pluchart, the sliced roots are submitted to fermentation without previous extraction of the juice, and also without addition of yeast, the alcohol being afterwards distilled from the sliced roots with the aid of steam.

Spirits from the By-Products of Sugar Manufacture. In the East Indies the scum from the boiled sugar, the molasses, &c., are brought to fermentation and the fermented fluid distilled. The product is in the English colonies known as *Rum*, in Madagascar and the Isle of France as *Guildine*. The peculiar aroma of rum is contained in the portion which first distils over. By the fermentation and distillation of the scum from the boiling of the sugar-cane juice, a coarse, sour, dark brown or black-coloured acrid tasting brandy is obtained; it is known as *Negro rum*. In England and Germany rum is frequently made from the diluted molasses of the sugar refineries fermented with yeast, the fermented fluid being distilled after about 3 to 4 days' fermentation. The aroma peculiar to rum is obtained by the addition of some pelargonic ether or essence of pine-apple. Beet-root molasses are also largely used for the purpose of obtaining spirits. By itself the beet-root sugar molasses are difficult to ferment, but if the alkalinity of this material is first neutralised by the addition of some sulphuric acid, and the material next boiled with a further addition of acid for the purpose of converting the cane sugar it yet may happen to contain into inverted sugar, the fermentation may be readily set up and regularly proceed. 100 kilos. of molasses yield on an average 40 litres of spirit. The very objectionable odour of this spirit is due to fusel oil, which contains small quantities of propylic, butylic, and amylic alcohol, pelargonic acid, and caprylic acid, while later researches have added to this list œnanthic, caproic, and valerianic acids. The residue left in the retort is used for the preparation of potassa (see page 118). The addition of sulphuric acid has not only the effect of converting the cane sugar into an easily fermentable sugar, but also prevents the setting up of lactic acid fermentation.

Spirits from Wine and Marc. The distillation of spirits from wine is chiefly carried on in France, Spain, and Portugal. The yearly production of spirits from wine or French brandy (*alcool de vin*) in France alone, amounts to 450,000 hectolitres of 85 per cent., and 400,000 hectolitres of 60 per cent. The quality of the spirit is indirectly affected by the degree of ripeness of the grapes, and directly by the care bestowed upon the fermentation and distillation, the more or less intimate mixture of the volatile principles of the wine with the alcohol, and by the age of the wine. Old wine yields a spirit of better quality than new wine. The freshly distilled brandy is colourless, and remains so even when bottled; but since the spirit is kept in oaken casks it extracts therefrom some colouring and extractive matter. The best kinds of brandy are distilled in the Département de Charente, and the brand known in commerce as *Cognac* (name of a town) is the most valued. From the marc and wine-lees spirit is also distilled. By the distillation of spirits from wine a residue is left in the retort (the *vinasse*) which contains a large quantity of glycerine which may thus be obtained as a by-product.

b. Distillation of the Vinous Mash.

Distillation of the Mash. The fermented mash (as obtained from potatoes is a mixture or non-volatile and volatile substances. To the first belongs the fibre, malt, husks, inorganic salts, protein substances, undecomposed and decomposed yeast, succinic acid, lactic acid, glycerine, &c.; to the volatile, the alcohol, fusel oil, water, and small quantities of acetic acid. The volatile constituents of the mash, the products of the fermentation, are separated from the non-volatile by distillation, during which the volatile constituents are converted into vapour afterwards cooled and condensed in another vessel. When a vinous mash is heated to the boiling-point, vapours are generated which consist essentially of alcohol and water; by condensing these vapours there is obtained a mixture of alcohol and water.

Water boils at + 100° C., barometer 760 mm.
Alcohol ,, ,, + 78·3° C., ,, ,, ,,

Thus it might be thought that while the boiling-point of water is 21·70° C. higher than that of alcohol, it would follow that when a vinous mash is heated to 80° C., only the alcohol would be converted into vapour, the water remaining behind. But this is not the case, for under all circumstances the boiling-point of a mixture of alcohol and water is higher than that of pure alcohol alone, and the vapour formed consists of both alcohol and water. The reason is partly due to the affinity of alcohol for water, partly also to the fact that water evaporates at a lower temperature than its boiling-point; the former (affinity) retains alcohol and prevents it to escape at proper boiling-point (78·3°) in the shape of vapour. If the mixture of alcohol and water be heated to its boiling-point (suppose 90° C.) much more alcohol will be converted into vapour, because its boiling-point is lower, while of water only just so much is evaporated as would be the case were it when pure to be heated to this temperature, while simultaneously a current of air is passed through it, because the vapours of alcohol evolved from the mixture act exactly in the same manner as would a current of air carried through the mixture of alcohol and water, the former substance taking up just as much water as will be volatilised at the boiling-point of the mixed liquids. As the quantity of vapour evolved from a liquid bears a direct relation to the temperature of that liquid, the quantity of aqueous vapours in the mixture of vapours will increase according to the increase of temperature, until at last, as soon as the boiling-point rises to that of water (= 100°) no more alcohol will be present in the vapours which are given off. At the commencement of the distillation the vapour given off contains much alcohol and very little water; presently more water comes over, and finally only water. It is therefore quite evident that we cannot by distillation separate alcohol at once from the rest of the volatile constituents of a vinous mash liquor. By interrupting the distillation at the proper time, there is obtained in the distillate all the alcohol contained in the mash along with a certain quantity of water, while the residue of the distillation will not contain any trace even of alcohol. The liquor obtained by the first distillation is generally very weak alcohol, and requires further rectification, as it is termed, to increase the proportion of alcohol. This rectification (another process of distillation) may be continued till the alcohol contains only a small quantity of water, which can only be eliminated by the aid of such substances as have a greater affinity for water than the alcohol, which retains that liquid very tenaciously. Anhydrous, or absolute alcohol, can only be obtained by treating highly rectified alcohol with some substances which have a great affinity for water, such as caustic lime, fused chloride of calcium, &c.; but really absolute alcohol is never used on the large scale in industry. The first portions of liquid obtained by the distillation of vinous mash are rich in alcohol, and termed fore-run or first-run, while the last portions of the fluid yet containing alcohol are termed after-run. A doubly-rectified alcohol contains 50 per cent. pure spirit; but by means of rectification alone a stronger alcohol than of 95 per cent. cannot be obtained. The residue of the distillation is called fluid-wash.

The Distilling Apparatus. A distilling apparatus as usually employed consists in its simplest form of four parts, namely, the still or retort, the head or cap of the still, the cooling apparatus, and the receiver.

The still or retort is generally constructed of sheet copper—more rarely of iron boiler-plates. The shape of the vessel varies, but is generally a somewhat flattened cylinder, provided with a round opening of 12 to 14 inches in diameter, fitted with a collar about 1 inch in height forming the neck, on which the cap or head is placed. The bottom of the still is either somewhat bulged inwards at the centre or is quite flat. The residue of the distillation is removed through a waste-pipe fitted with a stop-cock attached to the bottom of the vessel. From the cap or head a pipe conveys the volatilised alcohol to the receiver, while jutting obliquely from the top of the still is a pipe for the introduction of the mash. The head carries the vapours from the still into the cooling or condensing apparatus; although a simple tube might answer this purpose, it is preferred to make the head of the stills large and wide, not only for the purpose of separating any particles of mash which might happen to be carried off with the vapours of the boiling liquid, but also to obtain a distillate richer in alcohol, because an increased surface is favourable to the cooling of the vapours, whereby thus the aqueous vapour is first condensed; moreover, large heads are advantageous in case, by a rapid evolution of vapours, the mash might boil up (priming); roomy space in the head prevents then the liquid passing over into the worm. Since the volume of the vapours decreases during the condensation, a somewhat conically-shaped head would be the best form for this portion of the apparatus. The cooling apparatus is not simply destined to convert the vapours carried into it from the head into liquid, but it is also required that this liquid be so far cooled down as to prevent—at least as much as possible—the evaporation of the distillate; the condensing apparatus should not be too roomy; that is to say, there should not be too much space for the vapours, because this would cause air to enter the cooling apparatus, and this air, while mixing with the vapours of alcohol, carries off along with it some of this fluid, thereby causing a loss of the fluid. It is also requisite that the cooling apparatus be strongly made, yet at the same time so constructed as to admit of being readily taken down for cleansing purposes and easily fitted up again; usually the cooling apparatus—technically termed worm—consists of a series of spirally bent tubes made of either block-tin or copper, seldom of lead; this apparatus is placed in a large wooden or metal vat containing cold water, or as in the more recently constructed distilling apparatus, cold vinous mash, which is thus made warm previous to being transferred into the still, whereby of course a saving of fuel is effected.

Improved Distilling Apparatus. However much the shape and details of construction of the apparatus, with the aid of which strong alcohol can at once be obtained by one distillation, may vary, these apparatus all agree in this respect, that the mixture of vapours of alcohol on their way from the still to the condenser become continuously richer in alcohol, so that on reaching the cooling apparatus strong alcohol is the result of the operation. This result can be attained in two different ways, viz.:—

1. By causing the mixture of vapours to pass repeatedly through alcoholic liquids formed by the condensation of the vapours first given off; when afterwards the temperature increases in consequence of the continued rush of vapours into the liquid, a new process of distillation begins, the vapours generated by it being far richer in alcohol than when the first distillation took place (principle of *rectification*).

2. By so cooling the mixed vapour that the water only is condensed, the alcohol passing on as vapour (principle of *dephlegmation*).

When, in former days (sixty to sixty-five years ago), it was desired to prepare strong alcohol, a repeated process of distillation was adopted; this of course was a costly affair both as regards consumption of materials, fuel, &c., and loss of time. At the present day distillation apparatus are generally so arranged that by a kind of dissociation of the mixture of vapours, alcohol of any desired strength can be at once prepared.

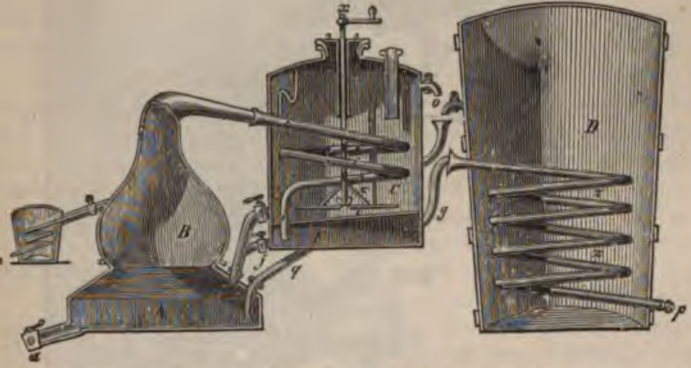
Most of the recent distillation apparatus may be considered to consist of the following parts:—

1. The still or vessel in which the fermented mash is placed.
2. Two condensing apparatus, one of which serves as rectifier, while the other completes the condensation of the products.
3. A dephlegmator in which the mixed vapour separates, a portion of the water becoming condensed and a vapour richer in the alcohol being carried on; this latter is carried into the cooling apparatus, while the former flows back into the still.

Among the many distilling apparatus employed in Germany for distilling fermented potato mash, we propose to describe those of Dorn, Pistorius, Gall, Schwarz, and Siemens.

Dorn's Apparatus. Dorn's apparatus, Fig. 233, consists of the still, A, the helm, B, which acts as dephlegmator, the condensing apparatus, D, and between the still and condensing apparatus, a copper vessel divided by a partition into two compartments, C and F, the upper of which, C, is termed the fore-warmer, the under, F, the rectificator. Connected with the helm is a small condenser, *n*, for the purpose of taking an occasional sample of the distillate which passes over. The fore-warmer is filled with mash to a level with the tube, *o*, and usually contains as much mash as is necessary to fill the still. With the help of the revolving arms, *x x*, the mash is from time to time kept stirred, and thus equally heated throughout to about 85° by the vapour passing through the pipe, *i i*, from the still. When the distillation is finished the wash (waste residue) is run off by opening the tap *a*, the still being re-filled with mash from the fore-warmer. As soon as the distillation commences the vapour is condensed in the worm, *i i*, the condensed fluid flowing into F. When the steam is no longer condensed in *i*, which occurs as soon as the mash has reached a certain temperature, the vapours pass over into the low wine, which thus becomes rapidly

FIG. 233.



heated to the boiling-point. By this means a second distillation is effected, really a rectification, the vapour or steam from which passing by the tube, *y*, is carried to the worm, *z z*, placed in the condenser, D, and having been converted into a fluid flows off at *p*. The distillation is continued until the fluid which comes over (the distillate) contains only 35 to 40 per cent of alcohol; a sample is then taken at the small cooling apparatus, K, to test the quality of the mash, and in order to ascertain whether it contains any more alcohol. When the distillate collected at *n* is found to be only water the operation is finished. The wash is run off from the still, and it is then re-filled with fresh mash from the fore-warmer through *l*, and

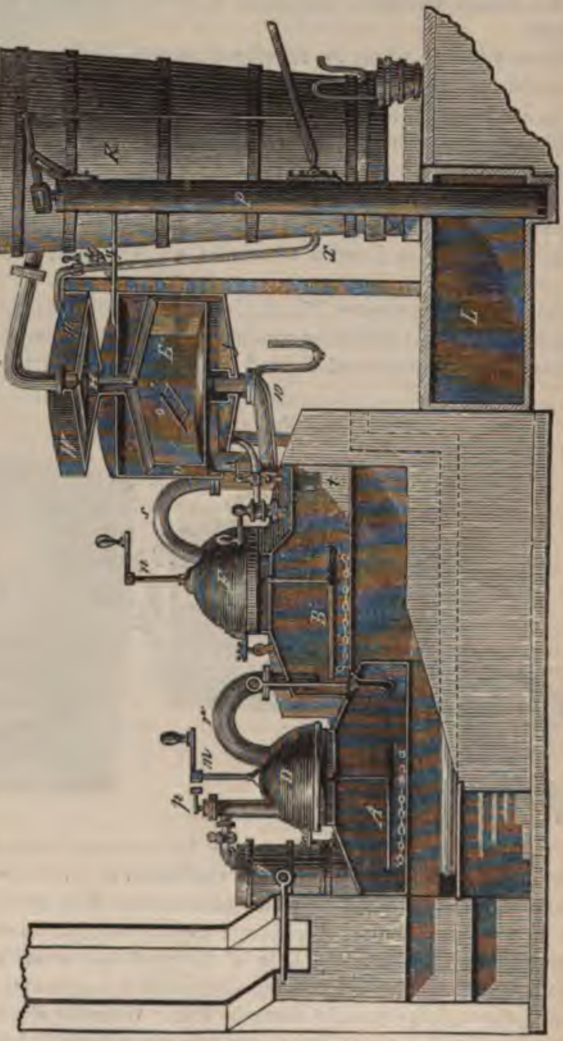


FIG. 234.

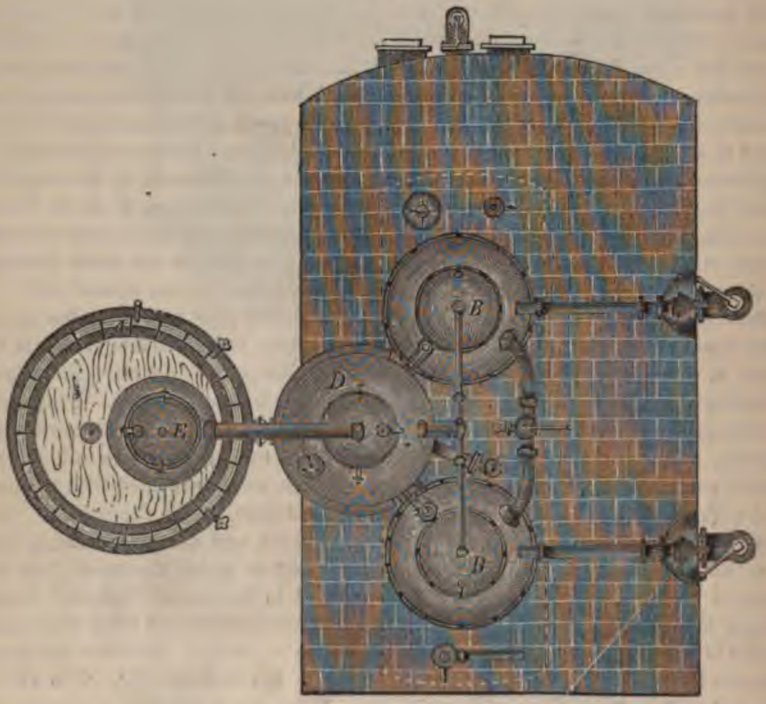
the distillation again proceeded with. The low wine contained in the vessel F flows through the tube *j* or *q* back into the still. As may be seen in the cut, Dorn's apparatus has not a separate dephlegmator and only one still or retort. This apparatus is now rarely used for distilling mash, but frequently for rectifying spirits.

Pistorius's Apparatus. Pistorius first introduced in Germany a distilling apparatus fitted with two stills ingeniously connected with rectificators and dephlegmators. When a distilling apparatus is required which not only extracts all the alcohol from the mash, but also produces the alcohol in a very pure and concentrated state, performing this work with the least possible expenditure of fuel and labour, Pistorius's apparatus answers the purpose admirably. A and B, Fig. 234, represent the two stills. A is the main still, which is either placed on a furnace and heated directly by fire or by means of steam. Heating by steam-pipes instead of direct firing possesses many advantages. The second still, B, is placed at a somewhat higher level than the first, and when not heated by steam-pipes is situated on the flue of the furnace fire of the first still. The main still, A, is fitted with a large helm, D, fastened on the still with bolts and nuts. *p* is a tube projecting from the helm and provided with a safety valve which opens inwards, in order to give access to air as soon as towards the end of the distillation a vacuum might ensue in the interior of the apparatus in consequence of the condensation of the vapours. There is also connected with this tube, *p*, a small condenser, *q*, as in Dorn's apparatus, from which samples showing the progress of the distillation may be taken. In both stills stirring apparatus, *m* and *n*, are fitted to prevent the mash burning. By the tube *x* the vapour of the "low wine" is admitted to the second still, the mash-still. From the helm, F, of the mash-still a curved pipe, *s*, conveys the vapour to the mash fore-warmer, which, as in Dorn's apparatus, is divided into two parts, the upper, E, containing the mash, the lower, *g* (the "low wine" cistern); the vapour ascending along the narrow passage, V, to the rectification apparatus, H. Frequently the vapour is conveyed to a third still before entering *g*; this still is not shown in the drawing. The rectification apparatus, H, consists of two or three conically-shaped vessels, made of sheet-copper and connected together, and is provided with a cistern filled with water, W; it is connected with the condenser, R, by the tube C. The tube *x* conveys cold water to the rectification apparatus, and the short tube, *y*, does so to the fore-warmer. The pump, P, is employed to pump the mash from the cistern, L, to the fore-warmer; thence it is carried to the second still, and thence again to the first still. When both stills and the fore-warmer are filled with mash, the fire is lighted under the first still. The steam or vapour from the mash in A passes to the mash in B, which is thereby heated to the boiling-point. The still B serves, therefore, the purpose of a rectificator. When the distillation has begun, the vessel, W, on the rectificator is filled with cold water, which is re-supplied when it has become warmed by the passing vapours. As soon as the steam reaches the upper rectificator, the real distillation commences. The condensed fluid drops into a cistern in which a hydrometer is placed.

Gall's Apparatus. In most apparatus for distilling from a vinous mash the distillate becomes gradually weaker and is not throughout of the same strength. Gall and Marienbad have endeavoured to avoid this defect in their apparatus, Figs. 235 and 236, so as to obtain a more uniform product during each distillation. Two stills are placed in a suitable manner in a steam-boiler and the stills are connected with the separator (low wine cistern). B B are the stills; C is a boiler with flues, *i i*.

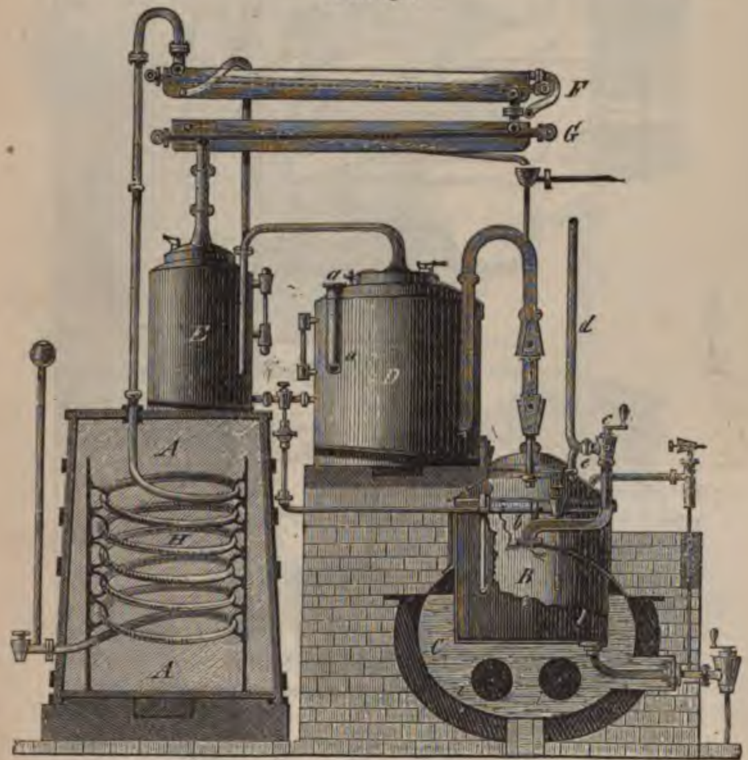
the stills, in order to prevent them cooling, are fixed into the boiler; D is a third still placed on, not in, the boiler; E is the low wine cistern; F and G two dephlegmators or separators; A is a condenser with a worm, H. The mash is put first into the still D by means of the tube *a a*, this still serving as a fore-warmer and rectificator. From this still both the stills B B are filled. From the boiler a current of steam is conveyed through the bent tube, *b*, into the three-way-cock, *c*, whence the steam is either passed into one or both the stills B B or is conveyed upwards by the tube *d* to the vessel destined to steam the potatoes. The vapour from one or both of the stills B B proceeds to the still D, and thence into the low wine cistern, E, and passing through the dephlegmators, F and G, finally enter into the condenser. The peculiarity of Gall's apparatus consists in that by the peculiar arrangement of tubes and stop-cocks, each of the two stills may at will be brought into action, it being possible to turn the steam at pleasure into the right-hand still, and next into the left-hand still, or *vice versa*. Each still may be also disconnected, the wash therefrom discharged and re-filled without in the least interrupting the working of the other portions of the apparatus; the distillation can therefore proceed uninterruptedly, one part of the apparatus being filled while the other is at work.

FIG. 235.



Schwarz's Apparatus. Schwarz's apparatus is in very general use in the south-west of Germany. It consists, Fig. 237, of the steam boiler, D; two mash stills, A and B; the fore-warmer, C; the "low wine" cistern, or receiver, E; the rectificators, H and F; and the condenser, G. M is a reservoir for cold. N one for hot water. The steam generated in the boiler, D, passes through the pipe, *g*, into the under compartment, A, of the double still, through the mash contained there; becoming mixed with vapours of alcohol, it arrives in the helm. *z*, and further makes its way by means of the tube *n* into the upper part of the double still; thence after a double rectification it is conveyed by means of the tube *t* to the fore warmer, C; the upper part of this vessel provided with the tubes *aaa* acts as a dephlegmator or separator, the condensed fluid flowing into E. The steam which arrives from the upper part of the still passes through E, and thence by way of the tubes *aa* into the helm, and the tube *n*, which latter is surrounded with the vessel H kept cold by means of cold

FIG. 236.



water; the dephlegmation continues here. From H the steam passes through V to F, an apparatus corresponding to the fore-warmer, C, but of smaller dimensions; because here the quantity of vapour has become greatly reduced while it has become richer in alcohol. The dephlegmator tubes are here surrounded by cold water, not by cold mash, the former liquid being constantly renewed so as to keep cold. The steam or vapour collected in the helm, *b*, is sufficiently laden with alcohol to admit of being at once conveyed to the condenser, G, the condensed distillate flowing out at *i*. The vinous mash is first poured into the fore-warmer, C, wherein it is occasionally stirred by the arms, *d d*, and crank, *d*, so as to keep it uniformly mixed and heated. When the mash has become warm it is conveyed into the upper compartment of the double still by the pipe, *e*, and into the lower compartment through the open valve; this compartment also serves as cistern for the phlegma from all other parts of the apparatus; the fluid flows backwards from the compartments *h* and *l* of the rectificators, H and F, by way of the tubes *m'* and *n*, into the low wine cistern, E, thence into the upper compartment of the double still, where it mixes with the mash. As soon as the mash has given up all its alcohol, which can be ascertained by testing the inflammability of the vapour issuing from the test stop-cock, *o*, the residue is

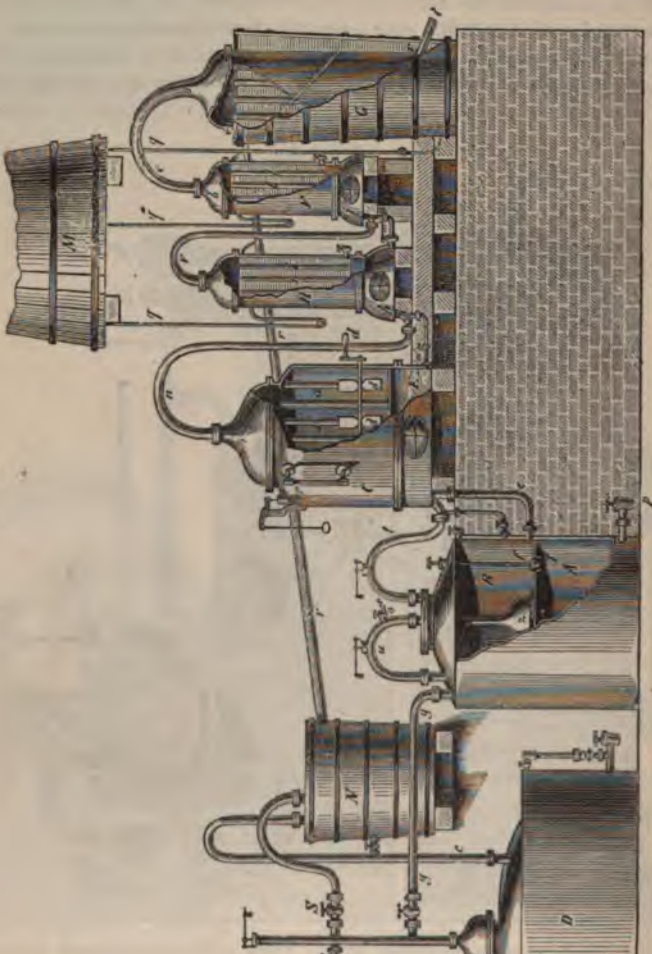
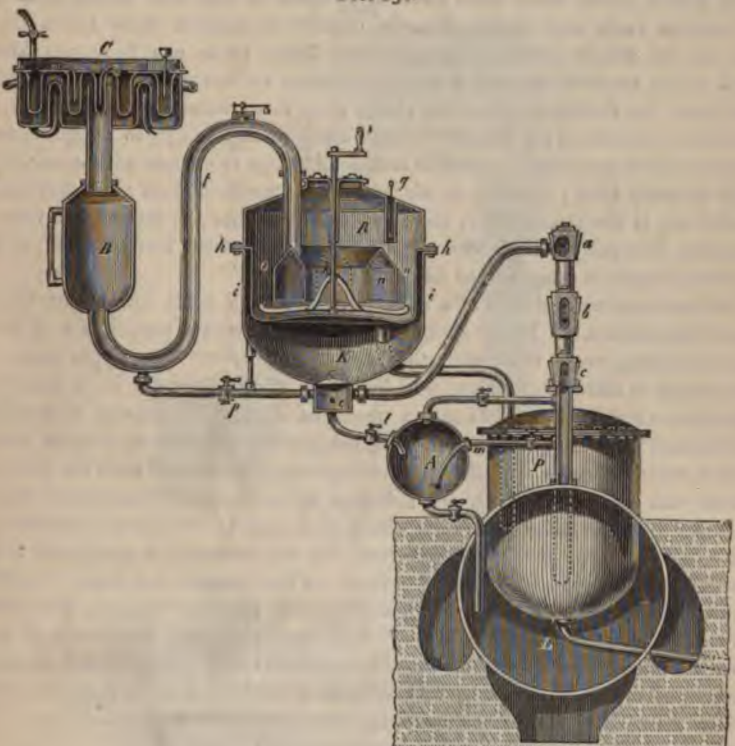


FIG. 237.

removed by opening the tap, *p*. By means of the tubes *q q q* the rectificators and condensing apparatus are supplied with cold water. The warm water from the condenser is conveyed by the tube *r* into the boiler. By means of R, the steam can be admitted to the potato vessels, and by S into the reservoir N, when it is desired to heat the water it contains to the boiling-point. Schwarz's apparatus possesses the advantage of being easily taken to pieces and cleansed. But, on the contrary, among its disadvantages are the following:—the construction of the mash-warmers is not quite suited for the purpose, while also the condensed liquid in E is not brought sufficiently into contact with the hot steam to affect a thorough distillation or rectification. The steam passes so quickly through the liquid that it is only very imperfectly deprived of its water (dephlegmated) when it reaches the dephlegmation apparatus, where it will consequently be but imperfectly rectified, while the vertical steam-pipes offer too few points of contact, and allow much steam to pass off without being fully condensed; while even the partly condensed vesicular steam is carried off along with the condensation escaping steam. The condenser itself is imperfect, being constructed of a number of vertical pipes, through which the condensed liquid rapidly falls without becoming quite cold, and in order to obtain a sufficient condensation an immense quantity of cold water has to be used.

FIG. 238.

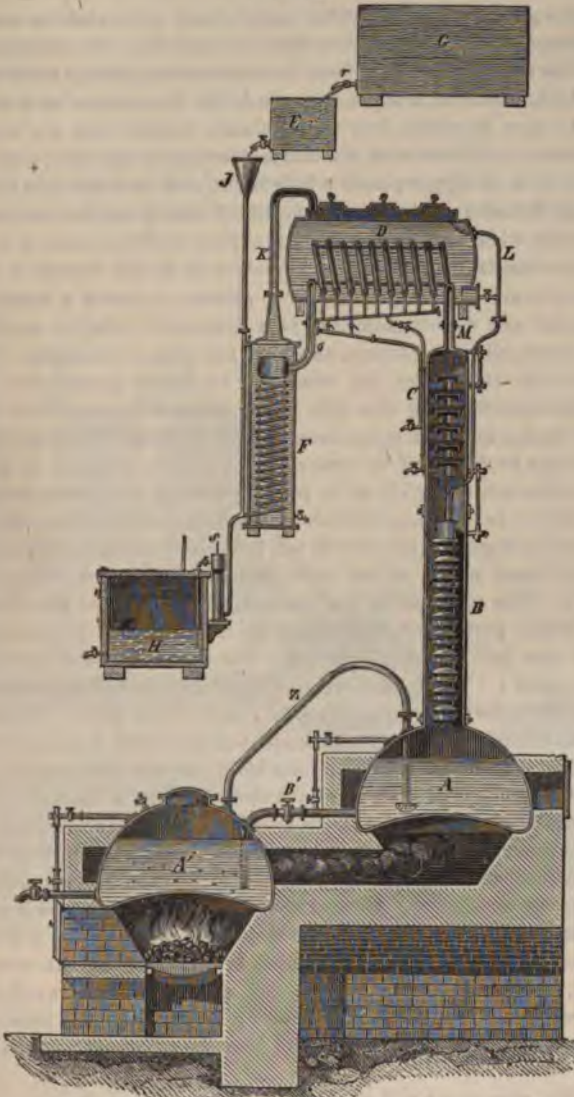


Siemens's Apparatus. Among the apparatus capable of producing a large quantity of spirits at a small cost is that of Siemens. This apparatus is much used in the distillation of brandy. It consists, Fig. 238, of two mash-stills set in a boiler, and capable of being alternately used (by means of the three cocks, *a*, *b*, and *c*), in the same manner as in Gall's apparatus, while the fore-warmer and dephlegmator is constructed according to Siemens's plan. L is the boiler; P one of the mash-retorts; K is the low wine receiver; R the fore-warmer; A, a reservoir in which the condensed water intended as feed water of the boiler is collected; C is the dephlegmator; B a reservoir for the vapours condensed in C. From the dephlegmator the vapour passes to a condenser not shown in the engraving. This apparatus is constructed of such dimensions that it can perform the work about to be mentioned. The boiler has to steam about 5000 kilos. of potatoes in four lots, during from 40 to 45 minutes each, and should thus be capable to yield in three hours the fifth part of the weight of the potatoes = 1000 kilos., or in one hour 333 kilos. of steam, which renders necessary a steam-generating surface of about 11 square metres. But since the distillation requires steam also, this generating surface has to be increased by about 20 per cent, and should consequently be 13·5 to 14 square metres. The size of the mash stills should be sufficiently large to contain with ease 500 litres when properly filled; because, as already stated, the fluid from A is not returned to the still but to the steam-boiler, the stills being set into the last-named vessel not becoming externally cooled, whereby the quantity of water carried along with the vapours of spirit is compensated for.

The mash warmer consists of a cylindrical portion, *i i*, the lower part of which has an indentation, *c*. In the cylinder is placed a narrower portion, *o o*, of the real mash-containing vessel fitted with the heating tube, *f n*. The upper part of the fore-warmer is fitted to the lower part by means of the flange, *h h*. *r* is a stirring apparatus, which is frequently set in operation during the process of distillation. The vapours from the second still are carried into the depression, *c*, under the fore-warmer, which in order that the vapours may come into contact with the phlegma is covered with a sieve. The vapours surround the under part of the mash reservoir and enter into the tube, *f*, through which they pass to the lower cylinder of the dephlegmator. The condensed water of the dephlegmator is conducted into the reservoir, A. The upper and under part of the fore-warmer are made of cast-iron, but the interior bottom and heating surfaces are made of copper. This kind of fore-warmer has the advantage of uniformly distributing the heat, while it can be easily cleansed. The dephlegmator, C, is so contrived that the rectified vapour can be conveyed to the condenser by two separate pipes placed in an opposite direction to each other, and are joined again in close proximity to the condenser. The remainder of the details will be seen on studying the drawing.

Continuous Distilling Apparatus. Among the distilling apparatus intended for the distillation of wine (not of mash), and so constructed as to be fit for continuous working, we must not neglect to mention the apparatus of Cellier-Blumenthal, as improved by Derosne, and represented in Fig. 239. This apparatus consists of two stills, A and A′; the first rectificator, B; the second rectificator, C; the wine warmer and dephlegmator, D; the condenser, F; the regulator, E; a contrivance for regulating the flow of the fluid wine from the cistern, G. The still A′, which as well as the still A is filled with wine, acts as a steam boiler. The low wine vapours evolved come, when they have arrived in the rectificators, in contact with an uninterrupted stream of wine, whereby dephlegmation is effected; the vapour thus enriched in alcohol becomes still stronger in the vessel D, and thence arrives at the cooling apparatus, F. In order that a real rectification should take place in the rectificators, the stream of wine should be heated to a certain temperature, which is imparted to it by the heating of the condenser water.

FIG. 239.

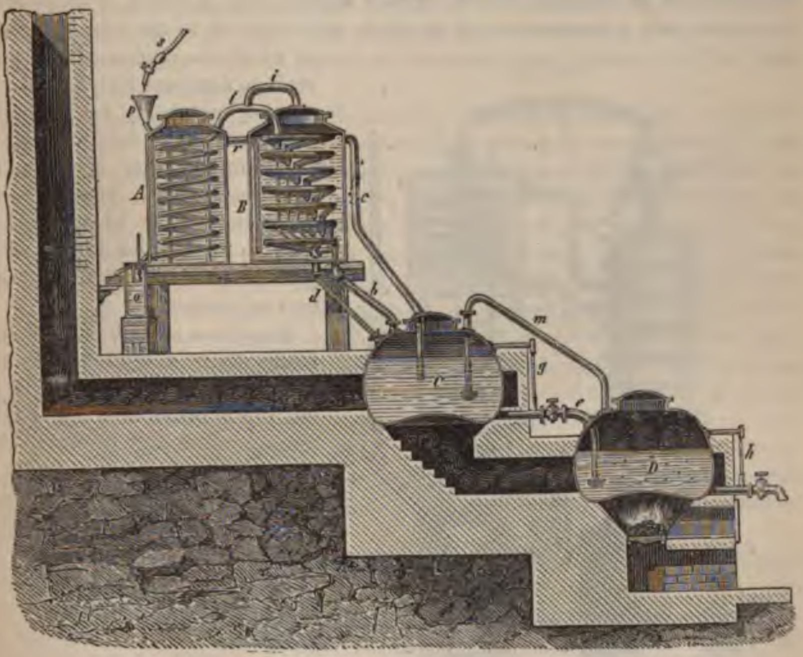


The steam from the still A' is carried by means of the pipe Z to the bottom of the still A. Both stills are heated by the fire of the same furnace. By means of the tube B' the liquid contained in the still A can be run into the still A'. The first rectificator, B, contains a number of semi-circular discs of unequal size, placed one above the other, and which are so fastened to a vertical centre rod that they can be easily removed and cleansed. The larger discs, perforated in the manner of sieves, are placed with their concave surfaces upwards. In consequence of this arrangement the vapours ascending from the stills meet with large surfaces moistened with wine, which, moreover, trickles downwards in the manner of a cascade from the discs, and comes, therefore, into very intimate contact with the vapours. The second rectificator, C, is fitted with six compartments; in the centre of each of the partition walls (iron or copper plates) a hole is cut, and over this hole by means of a vertical bar, is fastened an inverted cup, which nearly reaches to the bottom of the compartment wherein it is placed. As a portion of the vapours are condensed in these compartments the vapours are necessarily forced through a layer of low wine, and have to overcome a pressure of a column of liquid 2 centimetres high. The fore-warmer and dephlegmator, D, is a horizontal cylinder made of copper fitted with a worm, the convolutions of which are placed vertically. The tube M communicates with this worm, the other end of which passes to O. A phlegma collects in the convolutions of this tube, which is richer in alcohol in the foremost windings and weaker in those more remote: this fluid collecting in the lower part of the spirals may be drawn off by means of small tubes, thence to be transferred at the operator's pleasure, either all or in part, by the aid of another tube and stop-cocks to the tube O, or into the rectificator. By means of the tube L the previously-warmed wine of the dephlegmator can be run into the rectificator. The condenser, F, is a cylindrical vessel closed on all sides, and containing a worm communicating with the tube O. The other end of the condensing tube carries the distillate away. On the top of this portion of the apparatus the tube K is placed, by means of which wine is run into the dephlegmator. The cold wine flows into the cooling vessel by the tube I. When it is desired to work with this apparatus, the first thing to be done is the filling of the vessels A and A' with wine. The stop-cock, E, is then opened, whereby the tube J, the condenser, F, and the dephlegmator are filled with wine. The wine in the still A' is next heated to the boiling-point; the steam enters the tube Z and is condensed in A until the wine here is heated to the boiling-point by the combined effect of the steam and the hot gases circulating in the flue. The low wine vapour then passes to the rectificator, B, and thence into the worm of the dephlegmator, D, where the greater portion of it is condensed, the phlegma flowing backwards into the rectificator As soon as the fore-warmer is so far heated that the hand cannot be kept in the hot wine, the stop-cock of the vessel E is opened, and the distillation commences. The wine which is conveyed by the tube J into the cooling vessel, F, soon begins to become hot, and is then conveyed to the fore-warmer, where its temperature becomes nearly as high as the boiling-point; by means of the tube L this fluid is conveyed into the rectificator, B, and thence into the still A.

As soon as the wine in the still A' contains no more alcohol, the stop-cock, fitted to the lower part of the vessel is opened, and the vinasse run off at R, the still being re-supplied by opening the stop-cock, B'. The vapour proceeds in the same way, but in a reversed direction; when the vapour has been condensed in F it is first collected, as alcohol, in the small vessel, N, provided with an areometer, and thence conveyed to the cistern, H. The strength of the alcohol obtained by means of this apparatus increases with an increase of the number of the windings of the condenser placed in the dephlegmator and connected with the rectificator. Practical experience decides, according to the alcoholic strength of the wines to be distilled, and the quantity of pure alcohol desired in the distillate, the opening or shutting of the various stop-cocks of this apparatus. Derosne's apparatus may be readily made continuous; for this purpose it is only necessary to fill the reservoir, condensing apparatus, and rectificator with cold water, while the lower portion of the tube I is closed.

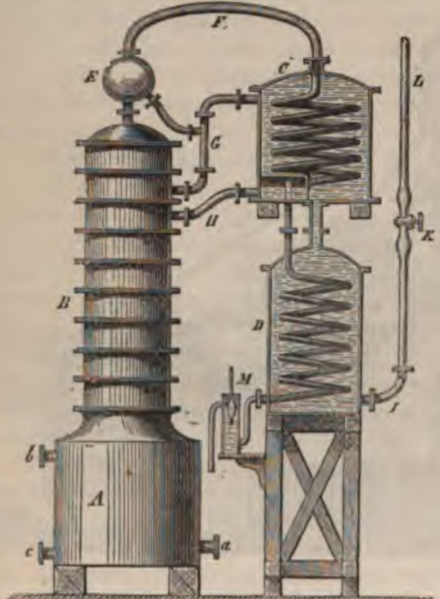
Laugier's Apparatus. Laugier's apparatus, shown in section in Fig. 240, is also of great interest. Notwithstanding the fact that Derosne's apparatus is exceedingly commendable for great economy of fuel, rapidity of distillation, and excellence of product, the apparatus is rather of a complicated construction, because it is arranged to distil all kinds of wine, be they weak or strong, while at the same time alcohol of any desired strength may be obtained. Apparatus of the construction of Laugier's, arranged for the distillation of one kind of fluid, wine or mash, and for the production of a distillate which is always of the same strength of alcohol, may be far more simply constructed. The fluid to be distilled flows from the tube, *s*, into the funnel, *p*, thence into the vessel A, entering its lower part and serving to

FIG. 240.



condense the alcoholic vapour. From this vessel the warmed fluid passes by means of the tube *r* into the lower part of the second vessel, B, where dephlegmation takes place by means of a condensing tube. Thence the fluid flows by way of the tube *c* into the second still, C, which is heated by the hot gases evolved from the fire kept burning under the first still, D; in the still C the fluid undergoes a rectification, and the vinasse flows by the tube *e* into the still D. M is the pipe conveying the hot vapour from D into C; the tube *b* conveys the alcoholic vapours into the dephlegmator. By means of the tube *d* the phlegma is conveyed into the still C; *f* serves as a means of emptying the still D; *g* and *h* are glass-gauging tubes for indicating the height of the fluid in the interior of the still; the tube *l* conveys the non-condensed vapours from the dephlegmator into the condensing apparatus; while *i* conveys the vapours formed in the vessel B into the condensing apparatus. The alcohol condensed in the cooling apparatus flows, as is exhibited in the cut, into a vessel, *o*, provided with an areometer to indicate the strength of the fluid. The cooling apparatus of the vessel B consists of seven compartments or divisions formed by wide spirals, each of which is at its lower level fitted with a narrow tube, all of which are connected to the tube *d*, by way of which the condensed fluids are made to flow back into the still. By properly regulating the boiling of the liquid in the first still and by adjusting the flow of wine, the condensation of the vapours in the dephlegmator can be arranged at will, so that either brandy of 50 per cent or alcohol of above 80 per cent be obtained.

FIG. 241.



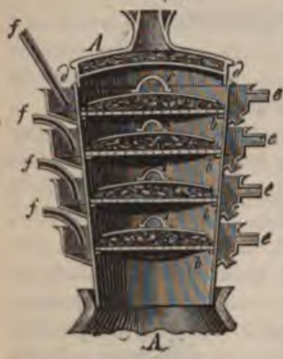
Sometimes an apparatus of even more simple construction is employed, in which the fluid to be distilled is heated by a spiral tube, through which high-pressure steam is made to circulate. Such an apparatus is exhibited in Fig. 241. A is a cast-iron or copper cylinder, in which the fluid to be distilled is heated by a spiral tube made of copper; the inlet of this tube is at *b*, and the outlet at *a*; by means of *c* the vinasse, devoid of alcohol, is run off. B is the dephlegmator, through which the fluid to be distilled continually flows in a downward direction, while the vapour of the low wine evolved in A ascends uninterruptedly. In order to increase the surface and points of contact the arrangement in the deplegmator is very different. The vapour ascends to the reservoir, E, and by way of the tube F enters the rectificator, C, which is arranged as usual; the condensed portion returning through H to the dephlegmator, while the uncondensed vapour passes on to the condenser of the vessel D there to become condensed and carried off through M. The fluid to be distilled is kept in a tank (not represented in the cut) placed higher than the apparatus, being conveyed to the latter by way of the tube L I fitted with the stop-cock K, so that the liquid arrives first in D, is next conveyed to C, thence through G into the dephlegmator, and lastly into the cylinder.

Removing the Fusel Oils. Defuseling. It has been already mentioned (see p. 431) that in addition to ethylic alcohol there are formed during vinous fermentation—under conditions not at all clearly understood nor scientifically elucidated—larger or smaller quantities of alcohols homologous with ethylic alcohol; such, as, for instance, propylic, butylic, amylic alcohols, which, when mixed with larger or smaller quantities of complex ethers, bear the name of fusel oil, a fluid which imparts to the ethylic alcohol (in the shape of brandy, gin, whiskey, &c.) a very unpleasant flavour, also rendering these spirits when crude very injurious to the human system. Fusel oil differs according to the nature of the mash, potatoes, grain, and beet-roots being used in its preparation. Fusel oil is formed in large quantity only when fermentation takes place at a high temperature in a concentrated saccharine fluid, while no tartaric acid is simultaneously present. A fluid which ferments at a low temperature and is very dilute does not yield fusel oil, at least no amylic alcohol, which also is never formed in such wines as have been fermented when tartaric acid has been present in the fermenting fluid.

As it is a property of all fusel oils that they are less volatile than water and alcohol, they are only condensed when brandy, gin, whiskey, &c., are distilled towards the end of the distillation; while as regards the distillation of the alcohol these oils are chiefly met with in the products of the condensation of the dephlegmators. A portion, however, of the fusel oils comes over along with the alcohol, and being very intimately mixed therewith is not readily removed from these fluids. Potato fusel oil is essentially amylic alcohol ($C_5H_{12}O$), a colourless, very mobile fluid of 0·818 sp. gr., of penetrating odour, provoking coughing, and of a burning taste; it boils at 133°. By means of oxidising agents, such as manganate and permanganate of potash, a mixture of sulphuric acid and bichromate of potash, or manganese as well as platinum black, amylic alcohol is converted into valerianic acid ($C_5H_{10}O_2$). By the action of acids this amylic alcohol is converted into peculiar kinds of ethers in the same manner as this effect is produced by acids upon ordinary (ethylic) alcohol. Some of the ethers thus formed exhibit a highly agreeable odour, and are therefore used in perfumery, and for the flavouring of sweetmeats, bon-bons, &c.

As for many of the applications of potato-spirit the fusel oil is a disadvantage, the spirit has therefore to be submitted to an operation of rectification whereby the fusel oil is got rid of. The suggestions which have been made for this purpose refer either to the destruction of the fusel oil by oxidation or the action of chlorine, or the masking of the oil and its conversion into less disagreeable compounds; partly also to a real removal of the fusel oil from the spirit. When the fusel oil containing spirit is rectified over chloride of lime (bleaching-powder), permanganate of potassa, &c., valerianate of fusel-ether is formed; but since the action of these reagents is not limited to the amylic alcohol but extends to the ethylic, it is very difficult to adjust the quantity of these reagents so that only the amylic alcohol be acted upon. If the spirits from which the fusel oil is to be removed are treated with a mixture of sulphuric acid and vinegar, there is formed, besides some acetic ether, acetate of amyl, $\left.\begin{matrix}C_2H_3O\\C_5H_{11}\end{matrix}\right\}O$, of a pleasant fruity flavour. Hydrochloric and nitric acids, also used to remove fusel oil, act in a somewhat similar manner. The most approved method of removing the fusel oil is by means of well-burnt charcoal (vegetable charcoal, charred peat, bone-black), which, when brought into contact with the crude spirit, absorbs the fusel oil mechanically. By the aid of charcoal, spirits and brandy (not when obtained from wine), are purified either in the state of vapour, or by digestion with the charcoal, and filtration at the ordinary temperature of the air; rectification at boiling temperature over charcoal is altogether unsuitable, owing to the fact that the fusel oil absorbed by the charcoal is again readily dissolved at that temperature. The charcoal to be employed is granulated and passed through a sieve in order to remove adhering dust. The granulated charcoal is placed in a copper cylinder, fitted at top and bottom with a perforated plate or disc; this cylinder is connected with the distilling apparatus between the dephlegmator and rectificator in such a manner that the vapours pass through the charcoal. To 100 litres of brandy to be purified 3 to 5 litres of granulated charcoal are generally required; this can be again employed after having been re-burnt at a bright red heat. Falkman's apparatus consists of a helm-shaped vessel, A, Fig. 242, in which the perforated diaphragms, *b b b*, are placed; upon each diaphragm a layer of charcoal, surmounted with a cover, *c*, is placed. The apparatus is closed with a hollow cover containing a layer of charcoal, *d d*. The vessel A is surrounded by a cooling apparatus, which in the cut is represented by the cold water tubes, *f f f*, and the hot water (which becomes hot by the passage of alcoholic vapours through A) tubes, *e e e e*; these serve the purpose of regulating the temperature of the layers of charcoal.

FIG. 242.



Yield of Alcohol. The quantity of alcohol obtainable from any given substance does not only depend on the relative quantity of the alcohol-forming constituents (starch, dextrose, or cane sugar) of the raw material applied for the purpose of distillation, but depends very largely also on the more or less suitable mode of conducting all the operations of the spirit distillation (mashing, fermentation), in properly constructed apparatus. Leaving out of the question the small quantities of glycerine and succinic acid formed by vinous fermentation, chemistry teaches that:—

100 parts of	starch	yield	56·78	of alcohol.
100 ,,	cane sugar	,,	53·80	,,
100 ,,	dextrose	,,	51·01	,,

Experience teaches that the yield of alcohol is in practice less than it should be, premising that every 1 mol. of starch or sugar yields 2 mols. of alcohol; 100 parts of cane sugar do not yield in practice the quantity of alcohol above indicated—viz. 53·8 parts, but only 51·1.

100	kilos. of	barley	give	44·64	litres	of	corn brandy	at	50° Tralles.
100	,,	barley-malt	,,	54·96	,,	,,	,,	,,	,,
100	,,	wheat	,,	49·22	,,	,,	,,	,,	,,
100	,,	rye	,,	45·80	,,	,,	,,	,,	,,
100	,,	potatoes	,,	18·32	,,		potato spirit	,,	,,

6 litres (quart or maas) of brandy, from the metrical hundredweight (hectolitre, &c.), is reckoned to yield 6 × 50 = 300 per cent alcohol; 7 litres, consequently, 350; 8 litres, 400. 8 litres at 48 per cent Tralles = 384 per cent alcohol. The number of litres of brandy or spirit multiplied by the alcohol in percentage according to Tralles therefore yield:—

1	metrical cwt. of	barley	44·64 × 50 = 2232	per cent	alcohol.
1	,, ,,	barley-malt	54·96 × 50 = 2748	,,	,,
1	,, ,,	wheat	49·22 × 50 = 2461	,,	,,
1	,, ,,	rye	45·80 × 50 = 2290	,,	,,
1	,, ,,	potatoes	18·32 × 50 = 916	,,	,,

Usually 1 Bavarian maas is taken as equal to 1·069 litres, 1 Prussian quart = 1·145 litres.

In quoting the prices in the following foreign markets, it is usual to take as a unit—

In Breslau	4,800	(60 quarts at 80°).
In Berlin	10,800	(200 ,, 54°).
In Magdeburg	14,400	(180 ,, 80°).

Recently it has become general to adopt as a unit 8000 (100 quarts at 80°).

Alcoholometry. For the purpose of ascertaining the quantity of alcohol contained in a fluid which consists only of alcohol and water, the areometer, or alcoholometer, is Areometer. generally employed. The vaporimeter and the ebullioscope (see p. 395) are seldom used. The application of the areometer is based upon the principle that a body immersed in a fluid (for instance, water) always displaces a quantity of water equal to its own volume, and loses in weight proportionately to the quantity of water displaced. It therefore follows, that by the depth to which the areometer sinks, as noted by the degrees on the spindle, we can determine the quantity of absolute alcohol contained in the fluid under examination. The areometer of Tralles and that of Richter are most generally used in Germany. Stoppani's is similar to that of Richter. Both are centesimal alcoholometers and show by the number of the degree to which they sink the percentage of pure alcohol. The difference between these two instruments consists in that the areometer of Tralles indicates percentage by volume, and Richter's percentage by weight. Tralles's alcoholometer is much used in the Zollverein (German Custom's Association, viz. of the various States constituting, with the exception of Luxemburg, the German Empire) for the purpose of ascertaining the alcohol contained in spirituous liquors (at 14·44° R.); in Austria the same instrument is used, with a difference, however, in the temperature at which the observation is made, the degree of the thermometer being usually taken at 12° R. (= 15° C.)

The following table exhibits a comparison of both scales, and with the true weight per cent, along with the corresponding specific gravity at a temperature of 15° C.:—

Sp. gr.	True weight per cent.	Approximate weight per cent according to Richter.	Percentage of volume according to Tralles.
0·990	4·99	5	6·23
0·981	11·11	10	13·73
0·972	18·12	15	22·20
0·964	24·83	20	30·16
0·956	29·82	25	36·50
0·947	35·29	30	42·12
0·937	40·66	35	48·00
0·926	46·00	40	53·66
0·915	51·02	45	58·82
0·906	54·85	50	62·65
0·899	60·34	55	67·96
0·883	64·79	60	72·12
0·872	69·79	65	76·66
0·862	74·66	70	80·36
0·850	78·81	75	84·43
0·838	83·72	80	88·34
0·827	88·36	85	91·85
0·815	92·54	90	95·05
0·805	96·77	95	97·55
0·795	99·60	100	99·75

The most usual alcoholometer is that which indicates the percentage of volume, or how many volumes of absolute alcohol there are contained in 100 volumes of the alcoholic fluid. Brandy of 50° Tralles is therefore understood to be a spirit, 100 litres of which contain 50 litres of alcohol; and from which by distillation these 50 litres of alcohol can be extracted. Considering that when alcohol and water are mixed a considerable contraction and decrease of bulk is the result, it is clear that 50 litres of alcohol (absolute is here meant) and 50 litres of water will only yield a mixture measuring 96·377 litres; and accordingly 100 litres of such a fluid contain instead of 50 litres of alcohol, 51·88 litres of that liquid.

Relation of Brandy Distilling to Agriculture.

The relation of the distillation industry to agriculture, and more especially as a means of providing fodder for cattle, is very interesting and important. The distillation of spirits leaves a residue which may be usefully employed as fodder for cattle; the distillatory process extracts from the starch-containing materials which are employed only the alcohol which is formed in the mash by fermentation, but it leaves behind in a concentrated state all the nutritive substances (especially albumen compounds), which not being acted upon by the fermentation, are left in the residues in almost the same state as they were originally present in the potatoes and grain made use of by the distiller. It is evident that when the expenses of the production of the spirits are paid to the distiller, the residues of the operation become a valuable material obtained cost free, the production of which is an important item in this industry.

Viewed in the light of agricultural industry the preparation of spirits from potatoes becomes in reality a chemical decomposition of the substances of which potatoes are composed, and a product of a relatively far greater value, and more readily transportable and preservable—viz., spirits and wash, and fodder material.

The Residue or Wash.

The wash is a fluid in which starch, dextrine, pectin substances, protein compounds, fat, small quantities of sugar, husks of grain, succinic acid, glycerine, salts, and some of the constituents of yeast are met with, partly in solution, partly suspended, while some of these materials are more or less decomposed and altered. The quantity of dry substance only amounts to from 4 to 10 per cent; this is due to the varying nature of the raw material, to the quantity of water used in mashing, and to the unequal quantity of water absorbed by the fermented mash during the process of distillation.

Ritthausen analysed several varieties of wash with the following results, the proportion of dry substance to the water being in (I.) as 1 : 7·3; in (II.) as 1 : 6; in (III.) as 1 : 4·08; in (IV.) as 1 : 4; in (V.) as 1 : 3:—

	I.	II.	III.	IV.	V.
Non-nitrogenous substances	2·78	3·23	3·08	4·14	5·31
Protein compounds	0·82	1·04	1·26	1·39	1·78
Cellulose	0·46	0·43	0·94	0·78	1·00
Ash	0·52	0·59	0·72	0·79	1·01
Water	95·40	94·71	94·00	92·90	90·90

When in a distillery potatoes and malt are always used in equal quantities and of the same quality, and the mash made at the same degree of concentration, the wash will always be of nearly as possible the same composition. It may be assumed that, on an average, three-fourths of the solid matter met with in the wash is nutritive; the proportion of nitrogenous to non-nitrogenous matter is on the average as 1 : 3, while in the potato it is only as 1 : 8. When the potatoes are converted into wash they lose the greater part of their non-nitrogenous matter, and thus become a fodder rich in protein compounds. In practice, 150 to 250 kilos. of potato mash are considered equivalent to 50 kilos. of hay.

Dry Yeast. By the fermentation of the beer-wort containing hops, yeast is produced in large quantities, and this is used in most cases when it is desired to induct a vinous fermentation; but for some purposes, such as bread-making for instance, this yeast is not applicable owing to its containing much of the bitter principle of the hop, and therefore possessing a very disagreeable flavour. This bitter principle may be removed by thoroughly washing with cold water, or, as recommended by Trommer, by first dissolving the yeast in a solution of caustic alkali, and then precipitating it therefrom by means of dilute sulphuric acid: such proceedings, however, always impair the efficacy of the yeast as a ferment, and the additional amount of time and labour required necessarily enhances the price of the yeast. The production of yeast in breweries is, moreover, only a subordinate affair, the main point being the preparation of beer of good quality. The production of yeast, although it can only be obtained by vinous fermentation, is best combined with the distillation of spirit, whereby, if desired, the preparation of dry yeast may be made a principal, and the production of spirit to a certain extent a subordinate, affair.

We have in a former portion of this work, while treating on fermentation in general, explained the mode of formation and the nature of the yeast, and that this yeast has been proved by experience to be best fed and most rapidly propagated by the gluten and other protein compounds of the cereals in solution. Yeast may be made in various ways. At Schiedam (Holland) it is made of excellent quality by a mode which is to a certain extent a trade secret—and differs materially from the following process:— A mash is made in the ordinary manner of 1 part of bruised barley malt with 3 parts of bruised rye, the mash being cooled with the fluid portion of the wash. To 100 kilos. of the bruised grain is added 0·5 kilo. of carbonate of soda and 0·35 kilo. of sulphuric acid diluted with water; these ingredients having been added to the mash it is brought to fermentation by the aid of yeast. The newly-formed yeast is removed from the strongly-fermenting fluid by the aid of perforated ladles it is then strained through a linen cloth or fine sieve, and poured into cold water, wherein it is allowed to form a sediment. The sediment thus produced is collected after the supernatant water has been run off, is placed in a stout canvas bag under a press, and formed into a stiff clayey dough, to which usually 4 to 1 (sometimes as much as 24) per cent of dry potato starch is added. Sometimes the water is removed from the yeast by placing that substance upon slabs made of gypsum or other absorbent materials, care being taken to keep the yeast in a cool place; by the use of the hydro-extractor—expressly arranged as regards its construction for this purpose—yeast may be very rapidly rendered dry. As regards the use of the carbonate of soda, it appears to assist in the separation of the glutinous constituents of the cereals; the action of the sulphuric acid is partly similar, and it also prevents the formation of lactic acid, which, if formed, causes a loss of both starch and spirit; the sulphuric acid also accelerates the separation of the yeast. According to communications by some of the most eminent distillers at Schiedam to Dr. G. J. Mulder, neither soda nor sulphuric acid are used at Schiedam in the preparation of what the trade terms dry or German yeast, some of which is imported into this country from Hamburg. Assuming the researches of Pasteur and others on fermentation to be correct, these observations are of great value in reference to the manufacture of yeast. It is found that the yeast sporulæ become properly developed when they are placed in a fluid which, instead of containing protein compounds, consists of aqueous saline solutions mixed with a sugar solution, such as, for instance—tartrate of ammonia, phosphate of potash, gypsum, phosphate of magnesia. It would hence appear that under such conditions yeast cells take up the material for the propagation of new cells, partly from inorganic substances, partly from organic, viz., the decomposing sugar which yields carbonic acid: in this respect the yeast cells agree, then, with higher organised plants. As regards the quantity of yeast obtainable from a given weight of materials, it may be stated that from 100 kilos. of rye, including the bruised malt, about 15 to 16 kilos. of dry yeast can be obtained. As the quantity of real yeast or of the nitrogenous matter for sale present in the ready prepared dry yeast amounts at the most to 20 per cent, the nutritive value of the wash obtained after the distilling off of the spirits from the fermented liquid is but little impaired.

So-called Artificial Yeast. We have yet to refer to what is termed artificial yeast, in reality a substance only intended for transferring the fermentation of the wort or mash in activity to-day to a fresh batch to-morrow, so that it bears the same relation to the spirit preparation as leaven does to bread-baking. There are a great number of recipes for the preparation of artificial yeast and of artificial fermentation-inducing substances; as far as these are known they may be brought to the following categories:—1. A small quantity of fully and strongly fermenting mash is mixed with fresh mash. 2. A small quantity of the fluid portion of the fermenting mash is cautiously drawn off by the aid of a syphon, and this portion having been set into fermentation, is added to the freshly made mash of the next day. 3. As soon as in the last-made mash the fermentation is strongest and most active, a small quantity of the ferment (yeast) separated from the fluid, and floating on its surface, is mixed with freshly made mash, the temperature of which has been purposely made sufficiently high to start the fermentation. The mash thus prepared may be used after a few hours to induce fermentation in a freshly made mash. A really artificial yeast, that is, yeast only prepared for the purpose of obtaining that substance by itself and independent of either brewing or distilling, is made in various ways, but always by a real process of fermentation. As an excellent instance of this mode of preparation, we quote the mode of preparing Vienna yeast:—

Vienna Yeast. This yeast is prepared in the following manner:—Previously-malted barley, maïs, and rye are ground up and mixed, next put into water at a temperature of 63° to 75°; after a few hours, the saccharine liquid is decanted from the dregs, and the clear liquid brought into a state of fermentation by the aid of some yeast. The fermentation becomes very strong, and, by the force of the carbonic acid which is evolved, the yeast globules (the size of which averages from 10 to 12 m.m.) are carried to the surface of the liquid, and, forming a thick scum, are removed by a skimmer, then placed on cloth filters, drained, washed with a little distilled water, and next pressed into any desired shape by means of hydraulic pressure, and covered with a strong and well woven canvas. This kind of yeast keeps for eight to fourteen days according to the season, and is, both for bakers and brewers, very superior to that ordinarily used; the extra good qualities of Vienna beer and bread are partly due to the use of this yeast in preparing these articles.

Duty on Spirits. In the original work a couple of pages are devoted to an uninteresting discussion on this subject, which, as might be expected, has been treated not from a general point of view but from one bearing upon conditions which are altogether different from those existing in this country. There can be no doubt that a duty on spirits is a very excellent thing; indeed, in this country this tax brings in such an enormous sum as to lead to the inference that spirits are consumed in larger quantities than is consistent with healthy conditions of body and social comfort.

BREAD BAKING.

Modes of Bread Making. The preparation of bread aims at the production in the flour obtained by grinding up the cereals of such a chemical and physical condition as will tend to render it most readily masticated by the teeth, and after having been duly mixed with saliva in the mouth, digested by the juices of the stomach. When flour is mixed with water so as to form a dough, and this mixture dried at the ordinary temperature of the atmosphere, a kind of cake is obtained which contains the starch unaltered and in an insoluble state, so that this kind of cake is very difficult to digest, while, moreover, its taste is so unpleasant as to create no appetite. Again, if the cake is dried at the boiling-point of water, it becomes like a dried starch paste, which is also very difficult to digest. When this temperature only acts upon the surface of such dough, and does not penetrate into the interior, the resulting cake will be a mixture somewhat similar to ship's biscuit, which may always be considered as a strongly-dried dough, and although it may be preserved for almost any length of time, it is far less digestible than bread. The object of the baking process is to impart to the dough so high a degree of heat as to render the starch soluble, while it is further desired to form a light spongy mass, instead of a brittle or watery paste; the heat should be strong enough to torrify and roast the outer surface of the bread mass to such an extent as to form a deeply coloured crust, whereby not only the taste of the bread is greatly improved, but it can also be kept in good condition for some time. The usual means of rendering dough spongy is by vinous fermentation set up by the addition of a ferment, this being either leaven or yeast; a small portion of the starch of the flour is thus converted into glucose, which is then decomposed, yielding alcohol and carbonic acid gas; the latter, while trying to escape, is prevented from doing so by the toughness of the dough, which is thereby rendered spongy.

The alcohol is of no consequence whatever. White bread is prepared with wheaten flour and yeast; rye meal or a mixture of rye meal and wheaten flour with leaven, yields "black" or rye bread. Heeren found that flour in the state in which it is usually applied for bread baking contains an average of 13 per cent moisture.

The Details of Bread Baking. The raw materials employed in the preparation of bread are flour, water, and a ferment, salt, spices, &c., are also used. The composition of the most important kinds of flour and meals is as follows:—

	a.	*b.*	*c.*	*d.*
Water	15·54	14·60	14·00	11·70
Albumen	1·34	1·56	1·20	1·24
Vegetable glue	1·76	2·92	3·60	3·25
Casein	0·37	0·90	1·34	0·15
Fibrin	5·19	7·36	8·24	14·84
Gluten	3·50	—	—	—
Sugar	2·33	3·46	3·04	2·19
Gum	6·25	4·10	6·33	2·81
Fat	1·07	1·80	2·23	5·67
Starch	63·64	64·28	53·15	58·13
Sand	—	—	6·85	—

a. Wheat flour. *b.* Rye meal. *c.* Barley meal. *d.* Oatmeal.

In addition to these kinds of meal, those derived from zea-maïs (Indian corn) beans, peas, &c., are occasionally employed for making bread.

The principal phases of the preparation are :—

The Mixing of the Dough and the Kneading. 1. The mixing of the flour with water is the first manipulation of the baking process. The object of this operation is first to render dextrin and sugar (owing to the action of the gluten upon the starch, the quantity of sugar becomes increased while the mixing process is going on) and some albuminous substances soluble, and next to mix the solution thus formed thoroughly with the starch and gluten of the flour, and to soak and somewhat dissociate these substances; dry yeast or leaven are at the same time added to the bread mass, the former ferment being used when it is intended to make white; the latter when black bread is desired to be made.

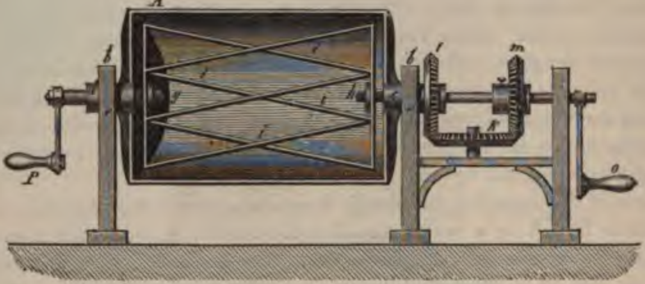
By sour dough or leaven is understood that portion of the already fermenting dough which is set apart and kept for the next baking operation; it consists of a mixture of flour and water, in which a portion of the starch is converted—partly into sugar, which is again changed by vinous fermentation, and acetic acid—but chiefly into lactic acid, by a process of fermentation set up by the peculiar conversion into active ferments of the protein compounds of the flour itself. Leaven therefore acts as a fermentation-producing substance in a fresh batch of dough, its action being similar to that of yeast, or of already fermenting wort when added to a freshly made wort. After a length of time the leaven becomes putrid and unfit for use as a ferment. As regards the quantity of leaven to be used with the dough nothing definite can be said, since it depends as much on the degree of sourness of the leaven as on the quality of the bread intended to be made; usually 4 parts of leaven are added to 100 parts of flour, or to 80 parts of bread 3 parts of leaven. In the case of white bread, 100 parts of flour require 2 parts of dry yeast. The mixing of the flour is effected with lukewarm water, at a temperature of from 21° to 37°.

Kneading. The thin dough obtained from flour, water, and ferment, is dredged over with dry flour, and placed in a warm situation for a time, generally during the night. Fermentation is thus set up by the action of the ferment upon the dextrose of the dough, the carbonic acid developed rendering the dough spongy. The sponge thus prepared, is next mixed with more flour to bring it to the consistency required for the baking, this operation being known as the kneading of the sponge. The method usually employed in these operations is that one-third of the total quantity of flour required for a batch is mixed first with water and ferment, and when this mass has come into full fermentation, the two other thirds of flour are kneaded up along with the sponge, sufficient water being added to form a normal dough. After the kneading operation the dough is again dredged over with some dry flour, and left in a warm situation for the purpose of becoming thoroughly spongy: for this continued fermentation only about half the time is required as for the first-mentioned fermentation. In most bakeries, however, this second fermentation is not proceeded with, but the dough is, immediately after having been kneaded, cut up and shaped into loaves.

By means of the kneading the dough becomes squeezed together, and has, therefore, again to be left in a warm situation for further fermentation, during which it heaves up and increases to double its size. The dough is generally put either into a basket or tied in a stout cloth, which is previously dusted over with bran to prevent the pasty mass adhering to the cloth. The bulk of the dough increases twofold. When rye bread is made, the dough is frequently moistened on its external surface with lukewarm water, applied by the aid of a brush, in order to prevent cracks in the outer coating of the dough by the evaporation of the water; just before putting the loaves into the oven this brushing over with water is repeated. The water softens the outer surface of the dough, and dissolves some of the dextrine it contains, which substance, after the evaporation of the water from the surface, remains as a glaze upon the crust of this kind of bread. When the loaves have risen sufficiently and exhale a vinous peculiar odour, it is time to commence the baking process. Since the bread loses considerably in weight during the baking, the baker must proportion so much dough to each loaf before baking as will yield the legal weight of the baked bread. The weight of dough to be proportioned to a loaf of a certain fixed weight varies according to the size of the loaf, but increases comparatively with decrease in the size of the loaf. The dough generally loses in baking about 25 per cent of its weight. The smaller the loaf, the more crust in proportion to crumb; and since the crust contains less moisture, and, consequently, weighs less than the crumb, the loss of weight is greater in a small than in a large loaf.

Kneading Machines. The kneading of the dough by hand is not only very heavy work, but is unhealthy and objectionable on account of being unclean; the uniform quality of the dough is, moreover, by no means to be depended upon. Although it is impossible to perform by machinery any labour which absolutely requires the touch of the human hand, bread-kneading machines have been introduced wherever the making of only one and the same kind of bread is required. Among the numerous kinds of machines invented for this purpose we select for description that of Clayton (see fig. 243.) The constituents of the dough are placed in the cylinder, A, mounted in the framework, *b b*, and provided with hollow axles, *c* and *d*, turning in their bearings at *e*. The interior of the cylinder is fitted with the framework, *f*, which may be made to revolve by aid of the axles *g* and *h*. The two halves of this framework are connected together by the diagonal knives, *i i*, which, when the machinery revolves, work up the dough; the trough or outer cylinder revolves in the opposite direction to the revolution of the framework. The crank, *o*, is connected with the axle of the trough or outer cylinder; the crank, *p* with that of the inner framework. As the two cranks are turned in opposite directions they impart opposite movements to trough and framework. The revolving of the machinery may be performed by one man by the aid of one crank, since the axle, *h*, of the crank, *o*, which is fitted to the inner frame by means of the hollow axle-tree, and revolves along with it, carries a conically-shaped wheel, *m*, fitted to the wheel *k*, which being connected with *l* causes the trough also to revolve; when, therefore, the wheel *m* turns towards the right, the wheel *t* will revolve towards the left.

FIG. 243.



The Oven. The conversion of the prepared dough into bread by baking is effected in an oven, ordinarily a circular or oval hearth or furnace, spanned by a vault, constructed with an opening at one end termed the mouth, serving alike for the introduction both of bread and of the fuel. The oven is built of bricks cemented together with fire-clay, the sole of the hearth being laid with tiles or lined with fire-clay. The vault is usually elliptical, in order to reflect the heat as much as possible. The mouth is closed with a door made of boiler-plate or of cast-iron; and as the mouth also serves as an exit for the smoke, a flue is constructed at some short distance above it, and made to communicate with the chimney. Two small openings in close proximity to the mouth of the oven serve to burn therein small pieces of wood to afford light, while the bread is being placed in the oven. The air necessary for the combustion of the fuel enters the oven from the lower part of the mouth, while from the upper the gases of combustion and the smoke escape. It is preferable, however, to construct these ovens with a separate flue and chimney communicating with another part of the vault, and to fit the flue with a damper to regulate the draught of the fire. Fig. 244 exhibits the vertical section, and Fig. 245 the plan of the sole of a baking oven. The sole, A, which is made so as to slope upwards towards the back of the oven, has a breadth of 3·1 metres, and a depth of 4 metres; it is spanned by a vault 0·5 metre high. The mouth is 0·8 metre wide. *e e e* are the flues through which the gases of combustion pass into the chimney, D, the draught being regulated by means of the damper, *u*. The trench, *x*, affords standing-room for the baker. Under the oven is a chamber serving as a store-room for the coal. The space E serves as a hot room wherein the bread is placed previous to being put into the oven in order that the dough may rise. Thoroughly dried wood is used as fuel; it is placed crosswise upon the hearth. Coals are used in England as fuel for this purpose. The oven has reached the required temperature, when a piece of wood rubbed on the hearth gives off sparks. The glowing charcoal is removed through the mouth of the oven, and extinguished in the lower chamber. Before the bread is put into the oven the sole is carefully cleaned with a wet swabber fastened to a pole, and ash and cinders having been removed the bread is put into the oven with the aid of an oven-shovel, fixed to a very long handle. The proper temperature of the oven for baking is between 200° and 225° C. Before the loaves are put into the oven they are brushed over with water wherein a small quantity of flour has been mixed, in order to prevent the crust of the bread formed by the first action of the heat flying off and cracking by the rapid expansion of the vapours formed by the heat to which the bread is exposed. The steam, which after some time fills the oven, materially assists the baking process, and very greatly aids the chemical changes which are especially apparent in the crust, which owes its glazed appearance thereto. The time necessary for the baking varies according to the size of the loaves, the form, and the kind of bread. The nearer the bread approaches to a globular form, and its surface therefore relatively smallest in relation to its contents, so much the longer time is necessary for the baking. Black bread takes a longer time to bake than white bread. These ovens are, however, not of the best construction: it is evident that they cannot be uniformly heated throughout, while they cool unequally also, and of course most so at the front part by the rushing in of cold air. After every batch of bread baked it therefore becomes necessary to fire the oven again for a short time

Fig. 244.

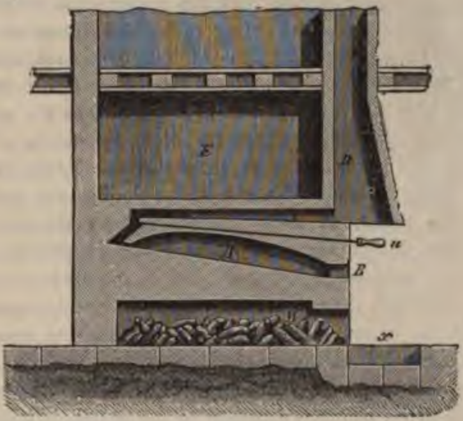
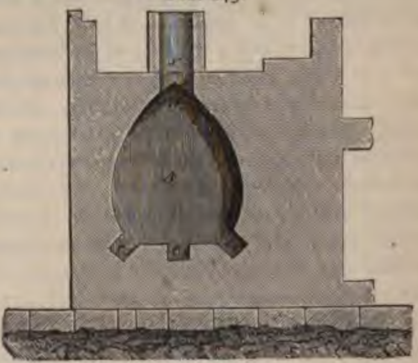


Fig. 245.



before a fresh batch of bread is put into it; of course less fuel is required to bring up the requisite temperature again than will be required when firing is commenced. When the baking of bread is carried on continuously and on a manufacturing scale, ovens are employed in which the baking- and the fire-rooms are separate and distinct.

Substitutes for the Ferments. *Substitutes for the Ferments in the "Raising" of Bread.*—We have seen from the preceding details that the preparation of bread is essentially based upon the fact that by the act of fermentation the gluten of the flour forms a kind of cellular tissue by which the escape of the carbonic acid is prevented, and thus the bread rendered porous and spongy, whereby its digestibility is increased. This quality of the bread is obtained at the cost of a portion of the starch of the flour, which is first converted into starch-sugar, and then by means of fermentation into alcohol and carbonic acid gas; to the expansion of the latter the bread owes its spongy texture. Many attempts have been made for the purpose of effecting the "raising" of the bread, as it is termed, without the use of a ferment, by introducing into the dough some gas- or vapour-producing substance, which would have the same mechanical effect at least as the carbonic acid derived from the fermentation. Although the problem of preparing bread of good quality without the aid of fermentation cannot be said to be quite settled, many proposals have been made in this direction, and some of these deserve notice; we therefore quote the most important. When sesquicarbonate of ammonia (the so-called *sal cornu cervi* of pharmacy) is added in small quantity to the dough, it will cause the raising of the same, partly because some acid is always present in the dough, whereby the salt is decomposed and carbonic acid set free, partly because by the heat of the oven the salt is volatilised, and by assuming the state of vapour causes the expansion and consequent sponginess of the dough. Liebig recommends the addition of bicarbonate of soda and hydrochloric acid to the dough, the carbonic acid being evolved according to the formula ($NaHCO_3+HCl=NaCl+H_2O+CO_2$) with the formation of common salt which remains in the dough. The proportions are as follows:—To 100 kilos. of meal for making black bread 1 kilo. of bicarbonate of soda is taken, and 4·25 kilos. of hydrochloric acid of 1·063 sp. gr. (=9·5° B.=13 per cent ClH), yielding 1·75 to 2 kilos. of common salt; the quantity of water to be added amounts to from 79 to 80 litres. From this mixture is obtained 150 kilos. of bread. The proportion of the bicarbonate of soda to the hydrochloric acid is so arranged that 5 grms. of the former are fully saturated by 33 c.c. of the latter, leaving in the bread a faintly acid reaction. The substance known and sold as Horsford's yeast powder, also recommended by Liebig, is preferable and more readily applied. This powder consists of two separate preparations, viz., the acid powder (acid phosphate of lime with acid phosphate of magnesia), the other the alkali powder (a mixture of 500 grms. of bicarbonate of soda and 443 grms. of chloride of potassium). To 100 kilos. of flour, 2·6 kilos. of the acid powder, and 1·6 kilos. of the alkali powder are added. During the kneading the following changes occur: the bicarbonate of soda and chloride of potassium are first converted into chloride of sodium and bicarbonate of potash, the latter salt being in its turn decomposed by the acid phosphate, whereby carbonic acid is set free. By the use of this baking powder it is possible to make flour into bread within two hour's time, while, moreover, 100 pounds of flour yield 10 to 12 per cent more bread than with the best method of baking in the usual way. The plan of incorporating pure carbonic acid gas with the dough has been frequently taken up and abandoned again; many trials have been made in this direction, and the process has its opponents as well as its defenders. Of later years the late Dr. Dauglish and Mr. Bousfield have taken this subject up, and after having obtained a patent have started the Aërated Bread Company. This process as carried out in practice is best described by an extract from Dr. Dauglish's pamphlet, using his own words:—

"I first prepare the water which is to be used in forming the dough by placing it in a strong vessel capable of bearing a high pressure, and forcing carbonic acid into it to the extent of ten or twelve atmospheres, taking advantage of the well-known capacity of water for absorbing carbonic acid, whatever its density, in quantities equal to its own bulk. The water so prepared will of course retain the carbonic acid in solution so long as it is retained in a close vessel under the same pressure. I therefore place the flour and salt of which the dough is to be formed also in a close vessel capable of bearing a high pressure. Within this vessel, which is of a spheroidal form, a simply constructed kneading apparatus is fixed, working from without through a closely packed stuffing box. Into this vessel I force an equal pressure to that which is maintained on the aërated water vessel; and then, by means of a pipe connecting the two vessels, I draw the water into the flour and set the kneading apparatus to work at the same time. By this arrangement the water acts simply as limpid water among the flour, the flour and water are mixed and kneaded together into paste, and to such an extent as shall give it the necessary tenacity. After this is accomplished the pressure is released, the gas escapes from the water, and in doing so raises the dough in the most beautiful and expeditious manner. It will be quite unnecessary for me to point out how perfect must be the mechanical structure that results from this method of raising dough. In the first place, the mixing and kneading of the flour and water together, before any vesicular property is imparted to the mass, render the most complete incorporation of the flour and water a matter of very easy accomplishment; and this being secured, it is evident that the gas which forms the vesicle, or sponge, when it is released, must be dispersed through the mass in a manner which no other method—fermentation not excepted—could accomplish. But besides the advantages of kneading the dough before the vesicle is formed, in the manner above-mentioned, there is another and perhaps a more important one from what it is likely to effect by giving scope to the introduction of new materials into bread making; and that is, I find that powerful machine kneading continued for several minutes has the effect of imparting to the dough tenacity or toughness. In Messrs. Carr and Co.'s machine, at Carlisle, we have kneaded some wheaten dough for half-an-hour, and the result has been that the dough has been so tough that it resembled bird-lime, and it was with difficulty pulled to pieces with the hand. Other materials, such as rye, barley, &c., are affected in the same manner; so that by thus kneading I am able to impart to dough, made from materials which otherwise would not have made light bread, from their wanting that quality in their gluten which is capable of holding or retaining, the same degree of lightness which no other method is capable of effecting. And I am sanguine of being able to make from rye, barley, oatmeal, and other wholesome and nutritious substances, bread as light and sweet as the finest wheaten bread. One reason why my process makes a bread so different from all other processes where fermentation is not followed is, that I am enabled to knead the bread to any extent without spoiling its vesicular property, whilst all other unfermented breads are merely mixed, not kneaded. The property thus imparted to my bread by kneading renders it less dependent on being placed immediately in the oven. It certainly cannot gain by being allowed to stand after the dough is formed; but it bears well the necessary standing and waiting required for preparing the loaves for baking.

"There is one point which requires care in my process, and that is the baking: as the dough is excessively cold, first, because cold water is used in the process, and next because of its sudden expansion on rising. It is thus placed in the oven some 40° F. in temperature lower than the ordinary fermented bread. This, together with its slow springing until it reaches the boiling-point, renders it essential that the top crust shall not be formed until the very last moment. Thus, I have been obliged to have ovens constructed which are heated through the bottom, and are furnished with means of regulating the heat of the top, so that the bread is cooked through the bottom; and, just at the last, the top heat is put on and the top crust formed.

"With regard to the gain effected by saving the loss of fermentation, I may state what must be evident, that the weight of the dough is always exactly the sum of the weight of flour, water, and salt put into the mixing vessel, and that in all our experiments at Carlisle we invariably made 118 loaves from the same weight of flour which by fermentation made only 105 and 106. Our advantage in gain over fermentation can only be equal to the loss of fermentation. As there has been considerable difference of opinion among men of science with respect to the amount of this loss—some stating it to be as high as 17½ per cent and others so low as 1 per cent—I will here say a few words on the subject. Those who have stated the loss to be as high as 17½ per cent have, in support of their position, pointed to the extra yield from the same flour of bread when made by non-fermentation compared with that made by fermentation. Whilst those who have opposed this assertion, and stated the loss to be but 1 per cent or little more, have declared the gain in weight to be simply a gain of extra water, and have based their calculations of loss on the destruction of material caused by the generation of the necessary quantity of carbonic acid to render the bread light. Starting, then, with the assumption that light bread contains in bulk half solid matter and half aëriform, they have calculated that this quantity of aëriform matter is obtained by a destruction of but 1 per cent of solid material. In this calculation the loss of carbonic acid, by its escape through the mass of dough during the process of fermentation and manufacture, does not appear to have been taken into account, that our calculations may be correct.

"One of the strongest proofs that the escape of gas through ordinary soft bread dough is very large arises from the fact, that when biscuit dough, in which there is a mixture of fatty matter, is prepared by my process, about half the quantity of gas only is needed to obtain an equal amount of lightness with dough that is made of flour and water only, the fatty matter acting to prevent the escape of gas from the dough. Other matters will operate in a similar manner—boiled flour, for instance, added in small quantities. But the assumption that light bread is only half aëriform matter is altogether erroneous. Never before has there been so complete a method of testing what proportion the aëriform bears to the solid in light bread as that which my process affords. The mixing vessel at Messrs. Carr and Co's. Works, Carlisle, has an internal capacity of 10 bushels. When 3½ bushels of flour are put into this vessel, and formed into spongy bread dough, by my process it is quite full. And when flour is mixed with water into paste, the paste measures rather less than half the bulk of the original dry flour. This will, therefore, represent about 1⅛ bushels of solid matter expanded into 10 bushels of spongy dough, showing in the dough nearly 5 parts aëriform to 1 solid: and in all instances, if the baking of this dough has not been accomplished so as to secure the loaves to spring to at least double their size in the oven, they have always come out heavy bread when compared with the ordinary fermented loaves. This gives the relative proportion of aëriform to solid in light bread at least as 10 to 1, and at once raises the loss by fermentation from 1 to 10 per cent, without taking into account the loss of gas by its passage through the mass of dough.

"I may be allowed here to state, what will be evident to all, that the absence of everything but flour, water, and salt, must render it absolutely pure; that its sweetness cannot be equalled except by bread to which sweet materials are superadded; that, unlike all other unfermented bread, it makes excellent toast; and, on account of its high absorbent power, it makes the most delicious sop, puddings, &c., and also excellent poultices. Sop, pudding, and poultice made from this bread, however, differ somewhat from those made from fermented bread, in being somewhat richer or more glutinous. This arises from the fact of the gluten not having been changed or rendered soluble in the manner caused by fermentation; but that this is a good quality rather than a bad one is evident from the fact, that the richer and purer fermented bread is, the more glutinous are the sops, &c., made from it; and the poorer and more adulterated with alum it is, the freer the sops, &c., are of this quality."

It should be observed that the alcohol formed during the fermentation of the bread and volatilised by the heat of the oven, acts along with the carbonic acid in rendering the dough spongy; upon this action of the alcohol is based the application of rum or brandy, which in small quantities are added to pastry and puddings made with flour, suet, eggs, sugar, butter, &c.

Yield of Bread. As regards the quantity of bread obtained from a given quantity of flour, it varies according to the quality of the latter; 100 kilos. of flour usually yield from 125 to 135 kilos. of bread.

Composition of Bread. The flour from various kinds of grain contain in its ordinary air dry condition from 12 to 16 per cent of water; by its conversion into bread the flour takes up much more water. 100 pounds of fine wheaten flour combine with 50 pounds of water, and give 150 pounds of bread. The composition of the flour and of the bread is, therefore, as follows:—

	Wheaten Flour.	Wheaten Bread.
Dry flour	84	84
Water originally contained in the flour	16	16
Water added for making the dough ...	—	50
	100	150

According to Heeren, 100 pounds of wheaten flour yield at least 125 to 126 pounds of bread; 100 pounds of rye meal, 131 pounds of bread. Fresh wheaten bread contains 9 per cent of soluble starch and dextrin, 40 per cent of unchanged starch, 6·5 per cent of protein compounds, and from 40 to 45 per cent of water. As is generally known newly baked bread possesses a peculiar softness, and is at the same time tough; does not yield crumbs readily: after one or more days' keeping, the bread loses this softness, becomes dry, crumbles readily, and is then called stale or old bread; it is usually supposed that this change is due to a loss of water; but, according to the researches of Boussingault, stale bread contains just as much water as fresh bread; the alteration is solely due to a different molecular condition of the bread.

Impurities and Adulteration of Bread. When the flour intended for the preparation of bread is more or less decayed, the gluten it contains is thereby altered; the carbonic acid evolved during the fermentation of the bread does not render the dough spongy, but it becomes, owing to the altered state of the gluten, a more or less slimy mass, which yields a tough and far less white-coloured bread; in order to counteract this defect, and to impart a good appearance to the bread made from flour which has been damaged by damp, or by having been too closely confined in casks and thereby heated, the bakers in Belgium and Northern France (and may we not say of England too), add to the dough a small quantity of sulphate of copper, $\frac{1}{15000}$ to $\frac{1}{30000}$; the base of this salt combines with the gluten, forming therewith an insoluble compound, thus rendering the dough tough and white, and capable of taking a large quantity of water. In order to detect the sulphate of copper in the bread, a portion of the bread to be operated upon is first dried, then ignited, and the copper separated from the ash by gently washing away the lighter particles, leaving the metallic copper in the shape of small shining spangles. In England alum is very generally added to bread. In Germany the addition of sulphate of copper and alum (0·5 per cent) to bread is prohibited by law, but in some parts of that country leaven is kept in copper vessels, whereby verdigris is formed, the appearance of which is by no means disliked by the bakers.

THE MANUFACTURE OF VINEGAR.

Vinegar, and its Origin. The fluid known in common life as vinegar is essentially a mixture of acetic acid and water. Acetic acid, $C_2H_4O_2$. or $C_2H_3{O \atop H}\Big\}O$, consists, in its highest degree of concentration, in 100 parts, of—

Carbonic acid	24	40·0
Hydrogen	4	6·7
Oxygen	32	53·3
	60	100·0

and is formed by the oxidation of alcohol as well as by the dry distillation of cellulose.

As regards the first mode of formation, the process of the conversion of alcohol into acetic acid may be represented by the following formula:—

$$\left.\begin{array}{l}\text{1 mol. alcohol } C_2H_6O = 46 \\ \text{2 ,, oxygen } 2O = \underline{32}\end{array}\right\}\text{yield}\left\{\begin{array}{l}\text{1 mol. acetic acid } C_2H_4O_2 = 60 \\ \text{1 ,, water } H_2O = \underline{18}\end{array}\right.$$

$$78 \qquad\qquad\qquad\qquad 78$$

Accordingly 100 parts of alcohol should give 129·5 parts of acetic acid of the highest degree of concentration. The process of conversion is, however, by no means so simple as just mentioned, because the alcohol is not at once converted into acetic acid, but first converted into a body which contains less oxygen than the acetic acid, viz., aldehyde, C_2H_4O. The conversion of the alcohol into acetic acid may be elucidated in the following manner:—

Alcohol $C_2H_6O = 46$

Subtract $H_2 = 2$ — H_2 becomes, by the aid of O taken up from the air, oxidised to H_2O.

Remainder Aldehyde — $C_2H_4O = 44$

Add $O = 16$ from the air.

Result— Acetic acid — $C_2H_4O_2 = 60$

100 kilos. of alcohol therefore need 300 kilos. (= 2322 hectolitres) of air, containing 69 kilos. of oxygen, for the conversion of the alcohol into acetic acid. It is, however, evident, that in practice this quantity of air is insufficient, and only that portion of the oxygen which is in the state of ozone is capable of performing the duty of acetification. Alcoholic liquids, in order to become converted into vinegar, require the presence of a peculiar fungus (cryptogamic plant), known as *Mycoderma aceti*, which appears to act as the carrier of the oxygen of the air, which is also by it rendered active and given up to the alcohol.

The origin of vinegar or acetic acid as a product of the dry distillation of cellulose cannot be elucidated by a simple formula, because there are formed in addition to acetic acid a large number of other compounds, among which are gaseous and fluid hydrocarbons, wood spirit, aceton, creosote, oxyphenic acid, tar, &c., the relative quantity of which depends not only upon the temperature at which the distillation took place, but also upon the shape of the retorts used, the quantity of hygroscopic water contained in the wood, &c.

a. Preparation of Vinegar from Alcoholic Fluids.

Vinegar from Alcohol. When alcohol is left exposed to air or to pure oxygen it is not converted into acetic acid. Nevertheless the conversion is due to the alcohol becoming oxidised; therefore it is evident the alcohol must be placed under such conditions as are most favourable to the formation of vinegar. In this, as in many other chemico-technical processes, practical experience is the best teacher. The most important points are, of course, the preparation of vinegar in the shortest time with the least expenditure of alcohol. The conditions most favourable to the formation of vinegar on the large scale are the following:—

1. The alcoholic fluid—prepared from grape wine or fruit wine, fermented malt infusion, beer, and brandy—should be sufficiently diluted; it should contain not more than 10 per cent of alcohol. Experience has proved that fluids prepared by the direct application of alcoholic fermentation, viz. wine, beer, &c., are more readily converted into vinegar than mixtures of brandy or alcohol and water. But too great a dilution should be avoided; for although a liquid containing 3 per cent or less alcohol can be converted into vinegar, the acetification proceeds very slowly in so dilute liquids.

2. A suitable temperature—not above 36° C., not below 10° to 12° C. At a temperature of 7° C. and less the formation of vinegar no longer takes place, a fact usually overlooked when the advantages, of keeping beer and other fermented liquids in ice pits or very cool cellars are enumerated. Above 40° to 60° the acetification proceeds very rapidly, but there is a loss of alcohol and vinegar by evaporation.

3. A plentiful supply of air or oxygen to the alcoholic fluid and an intimate contact between the two. Small quantities of alcoholic fluid with an extended surface

are more readily converted into vinegar than large bulks of fluid, because the former present a larger number of points of contact.

4. The presence of substances which conduce to the formation of vinegar; they are as regards their action similar to the ferments, and are therefore called acetic acid or sour producing ferments; but the acetification is not a physiological process, as is vinous fermentation, but simply one of oxidation. The best ferment is vinegar, and all substances impregnated with it, such as for instance the so-called vinegar plant, the *Mycoderma aceti*; it was formerly thought that the vinegar mycoderms stood to alcohol and vinegar in the same relation as yeast stands to sugar and alcohol, but this opinion is correct only so far as the addition of *Mycoderma aceti* to an alcoholic fluid, as proved by Pasteur's experiments (1862), is alike in the action of small quantities of vinegar and other acetification-inducing substances upon wooden vats and chips of wood thoroughly impregnated with vinegar; many of these substances contain particles which are undergoing a process of oxidation (*molécule en mouvement*), and by coming into contact with alcohol they draw that fluid into a course of oxidation also. Pure acetic acid is therefore incapable of inducing acetification, but vinegar, on the contrary, is capable of doing so because it always contains smaller or larger quantities of the protein compounds alluded to; but unless these are in a peculiar state of activity they are useless; this is shown by platinum black and spongy platinum, both of which are capable of converting alcohol immediately into acetic acid. We may therefore conclude that, by the presence of *Mycoderma aceti* as well as of spongy platinum, the oxygen of the air is rendered active—ozonised—and that only ozonised oxygen is capable of converting alcohol into vinegar. Acetic acid is, therefore, an oxidation product, not one of the *Mycoderma*. A more accurate investigation of the behaviour of peroxide of hydrogen and other ozone-containing or producing materials with mixtures of alcohol and water, will no doubt lead to a better knowledge of the theory of acetification, and may lead also to a more rational and improved mode of vinegar making.

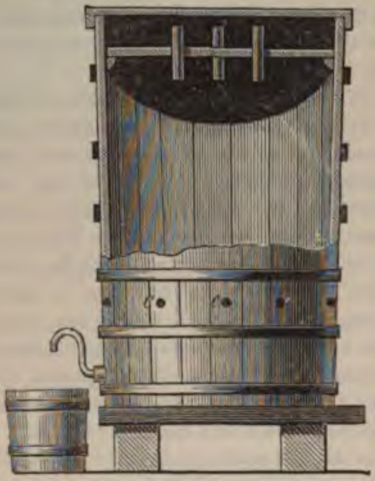
Phenomena of Vinegar Formation. Acetification exhibits phenomena which are important for observation because they indicate the progress of the conversion of the alcohol into acetic acid; these phenomena are partly of a chemical, partly of a physical kind. In proportion as the formation of vinegar advances, the alcoholic fluid loses its peculiar flavour and odour, and acquires the refreshing sour taste of vinegar. To the physical phenomena belong:—1. An increase in the specific gravity of the fluid; and (2) an increase of the temperature. The increase of temperature is due to the conversion of the oxygen from a gas to a fluid. The more active the absorption of oxygen the higher the temperature.

The Older Method of Vinegar Making. According to the substance from which vinegar is prepared the following kinds are distinguished:—1. Wine vinegar, prepared from wine, and containing in addition to acetic acid many of the other constituents of wine, namely, tartaric acid, succinic acid, and certain kinds of ethers, the latter imparting to wine vinegar its peculiarly agreeable flavour and odour. 2. Brandy vinegar, spirit vinegar, or artificial wine vinegar, generally only a mixture of acetic acid and water with a small quantity of acetic ether. 3. Fruit vinegar, prepared from cider and perry and containing acetic and malic acids. 4. Beer, malt, or grain vinegar, prepared from non-hopped beer wort, and containing, besides acetic acid, also extractive matters, such as, for instance, dextrin, nitrogenous constituents and phosphates. 5 Vinegar from the sugar beet-root. The roots are converted into a pulp and then pressed; the juice is next diluted with water and afterwards boiled. When sufficiently cooled, yeast is added and alcoholic fermentation set up; this having been finished the alcohol contained in the liquid is converted into vinegar. The vessel in which the acetification takes place is connected with a blowing fan; by the aid of a plentiful supply of air and the keeping up of a uniform temperature the alcoholic liquid to which some vinegar has been added is rapidly converted into acetic acid. 6. Vinegar prepared from the so-called wood vinegar or acetic acid obtained by the dry distillation of wood.

As regards the so-called old method of vinegar making it is without doubt an imitation of the spontaneous souring of beer, wine, and fermented liquors generally and on conditions which are conducive to the improvement of the product; such conditions are—a suitable temperature, intimate contact of the souring liquor with air, and a so-called acetification-inducing ferment. This method is very generally employed for making wine vinegar, French vinegar as it is termed in England, but may of course be used for malt or fruit vinegar making as well. Generally a "souring" vessel or "mother" vessel made of oak wood is employed; this vat is first, when newly made, thoroughly scalded with boiling hot water, and when thereby the extractive matter of the wood is exhausted the vessel is filled with boiling hot vinegar; when the wood is soaked with vinegar there is poured into the vessel 1 hectolitre of wine, and after eight days again 10 litres of wine are added, and this operation continued weekly until the vessel is filled for two-thirds of its cubic capacity. About fourteen days after the last addition of the wine the whole of the contents will have become converted into vinegar. Half this quantity is withdrawn from the souring vessel and carried to the store: to the remainder more wine is added, and the preparation of vinegar proceeded with uninterruptedly by the operation described. A souring vessel may continue to serve its purpose for six years, and often longer, but generally at the end of this time there is collected in the vessel so large a quantity of yeast sediment, argol, stone, and other matter as to render the thorough cleansing of the vessel necessary; after this operation it is again fit for further use. Although it might appear that in this process of acetification there is no great contact of air, and the fluid is apparently quite at rest, there is a constant change of the particles of the surface of the fluid, owing to the fact that every drop of vinegar formed sinks to the bottom of the vessel, or at least below the surface, owing to its increased specific gravity; while as regards the air, that portion of it from which the oxygen has been absorbed by becoming specifically lighter (0·9 sp. gr.) has a tendency to rise upwards, and to be replaced by heavier air (1·0 sp. gr.); thus a constant circulation of air is provided.

Quick Vinegar Making. The so-called quick vinegar process, founded on an older method of vinegar preparation suggested by Boerhaave in 1720, was first introduced by Schützenbach in 1823. The chief principle of this method consists in bringing the fluid, generally brandy, to be converted into vinegar into ultimate contact with the atmosphere at the requisite temperature, or, in other words, the oxidation of the alcohol to acetic acid is effected in the shortest time and with the least possible loss. The intimate contact of the fluid with the air is effected by:—1. Increasing the quantity of air admitted by means of a continual current of air being made to meet the drops of the fluid intended to be converted into vinegar in opposite direction to that in which these drops fall downwards. 2. By causing the liquid to be operated upon to trickle down drop by drop. A peculiarly constructed vessel is required for this operation; according to the strength of vinegar desired to be made two to four of these vessels are employed, these constituting a group or battery as it is termed. A sectional view of such a vessel is exhibited in Fig. 246; it is made of stout oaken staves, the vat being from 2 to 4 metres in height, and from 1 to 1·3 in width; at a height of from 20 to 30 centimetres from the bottom of the vessel are bored at equal distance from each other six holes—air holes—of about 3 centimetres in diameter, so cut that the inner mouth of the hole is situated a little deeper than the outer, that is to say, the holes are bored towards the bottom in a slightly sloping direction. About one-third of a metre above the real lower bottom a false bottom is placed, similar in construction to a sieve, and at a height of a centimetre above the air-holes; upon the false bottom is a layer of beech-wood shavings extending upwards to about from 15 to 20 centimetres below the upper edge of the vat. The false bottom is sometimes constructed of laths of wood, forming a kind of gridiron-like network. Before their application the wood shavings are thoroughly washed with hot water and next dried. The tub is then nearly filled with the dry wood shavings, which are next "soured." For this purpose warm vinegar is poured over them, and allowed to remain in contact with the wood for twenty-four hours so as to cause the acetic acid to soak into the wood. At from 18 to 24 centimetres below the upper edge of the vat is fixed a perforated wooden disc, the holes of which are as large as a goose-quill, and are bored from 3 to 5 centimetres apart from each other. In order that the liquid intended to be converted into acetic acid may trickle slowly, and in fine spray, as it were, over the wood shavings, or thin chips of wood, through the holes, strings of twine or loosely spun cotton yarn are passed so as to penetrate downwards for a length of 3 centimetres, while at the top a knot is tied which prevents the strings slipping through the holes; by the action of the liquid, dilute spirits of wine usually, which is poured into the vessel, the twine becomes more or less swollen, and thereby obstructs the passage of the fluid so as to divide it into constantly trickling drops. The sieve bottom is fitted with from five to eight larger holes, each about 3 to 6 centimetres wide, which by means of glass tubes, each of from 10 to 15 centimetres in length, inserted and firmly fastened therein act as draught tubes, so placed that no liquid can pass through them The vat is covered at the top with a tightly-fitting wooden lid, in the centre of which a circular hole is cut, which serves as well for the purpose of pouring the liquid into the vessel as for the outlet of the air which enters the vessel from below. In consequence of the absorption of the oxygen so

Fig. 246.

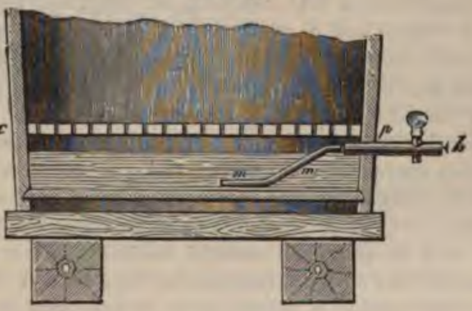


much heat is generated in the interior of the vessel that the air streams strongly upwards, causing fresh air to enter by the lower air-holes.

After the vinegar tub has been soured the fluid to be converted into vinegar—generally brandy, more rarely malt liquors or wine—is poured in; the fluid flowing off from the first vessel is poured into the second, and if the original liquid did not contain more than from 3 to 4 per cent of alcohol the fluid which runs off from the second vessel will be completely converted into good vinegar. The vinegar collects between the true and false bottoms. As will be seen from the woodcut the vinegar cannot flow out until its level is equal to that of the mouth of the glass tube. In consequence of this arrangement a layer of about 16 to 20 centimetres in depth of warm vinegar assists in the acetification by the evolution of acid vapours which ascend into the fluid above. The tube must dip into the lower part of the fluid in the interior of the tub, as it is there that the specifically heavier vinegar collects. The arrangement will be readily understood from Fig. 247. *c p* is the perforated bottom, just below which is situated the wooden tap, *h*, fastened to the bent glass tube, *m m*, the free open end of which touches the bottom of the tub.

Recently (1868) Singer's vinegar generator has been introduced. It consists of a number of vessels, one placed above the other, and so connected together by wooden tubes that the liquid intended to be converted into vinegar trickles drop by drop from the one vessel into the other; in each tube is cut a longitudinal slit, through which air freely circulates; the apparatus is placed in a suitably constructed shed, wherein a convenient temperature is kept up and from which draught is excluded. By the use of this apparatus the loss of alcohol experienced in the use of the vats above mentioned is prevented. Singer's apparatus is fully described in the "Jahresbericht der Chem. Technologie," 1868, p. 580.

FIG. 247.



The composition of the fluid to be acetified varies very much; one of the mixtures very generally used is made up of 20 litres of brandy of 50 per cent Tralles, 40 litres of vinegar, and 120 litres of water, to which is first added a liquid, made by soaking a mixture of bran and rye meal in water in order to promote the formation of the vinegar fungus (*Mycoderma aceti*). The room in which the vats are placed should be heated to 20° to 24°; the temperature in the vats rises to 36° and more, consequently the alcohol, aldehyde, and acetic acid are volatilised, and this loss may amount to about one-tenth; taking this loss into account we may assume that 1 hectolitre of brandy at 50 per cent Tralles (= 42 per cent according to weight) yields by weight—

13·0	hectolitres of	vinegar of	3	per cent	acetic acid	contents.
9·9	,,	,,	4	,,	,,	,,
7·9	,,	,,	5	,,	,,	,,
6·6	,,	,,	6	,,	,,	,,
5·6	,,	,,	7	,,	,,	,,
4·9	,,	,,	8	,,	,,	,,
4·4	,,	,,	9	,,	,,	,,
3·9	,,	,,	10	,,	,,	,,

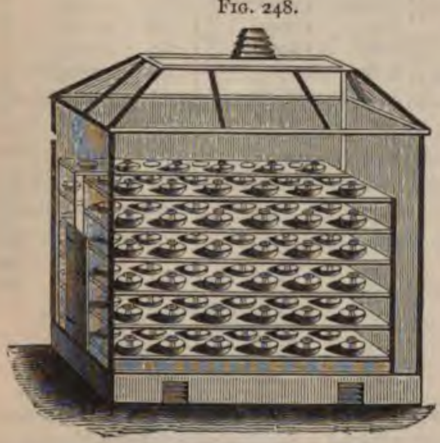
When required for transport it is, of course, most advantageous to prepare very strong vinegar, which at the place where it is to be consumed can be diluted with the requisite quantity of water.

Vinegar from the Sugar-Beet. Vinegar from the sugar-beet is prepared from the expressed juice, having a sp. gr. of 1·035 to 1·045, diluted with water to 1·025 sp. gr., fermented with yeast, the fluid being next mixed with an equal volume of prepared vinegar. This mixture being well exposed to the influence of the oxygen of the atmosphere, acetification soon sets in.

Vinegar with the Help of the Mycoderma Aceti. Pasteur, who refers acetification, as Dr. Wagner thinks erroneously, to a physiological process, has in 1862 described a new method of preparing vinegar with the help of the vinegar fungus, the *Mycoderma aceti*. This fungus is first propagated in a fluid, consisting of water and 2 per cent of alcohol with 1 per cent of vinegar and a small quantity of phosphate of potash lime and magnesia. The small plant soon spreads itself over the entire surface of the fluid, without leaving the smallest space uncovered. At the same time the alcohol is acetified. As soon as half of the alcohol is converted into vinegar, small quantities of wine or alcohol mixed with beer are added daily. When the acetification becomes weaker, the complete conversion of the free alcohol still present in the fluid is allowed to take place. The vinegar is then drawn off and the plant again employed in the same apparatus. Vinegar prepared by this method possesses much of the aroma characteristic of wine vinegar. An essential condition to the rapid formation of vinegar by this method is a strong development of the plant. A vessel with 1 square metre of surface, and capable of containing 50 to 100 litres of fluid, yields daily 5 to 6 litres of vinegar. The vessels are circular or rectangular wooden tanks, with but a slight depth, and covered with lids. At the ends are bored two small openings for the entrance of the air. Two tubes of gutta-percha, pierced laterally with small holes, are carried down to the bottom of the tank and used to pour alcohol into the tank without opening the lid. The tank which Pasteur employed had a surface of 1 square metre and a depth of 20 centims. He found phosphates and ammonia necessary for the growth of the plant. When wine or malt liquor, &c., is employed, these substances are present therein in sufficient quantity; but when only alcohol is used, sulphate of ammonia, phosphate of potash and magnesia are added in such quantity that the fluid contains $\frac{1}{10000}$th of this saline mixture, to which also some vinegar is added. It has been long known that the addition of bread, flour, malt, and raisins to alcoholic fluids about to be acetified greatly promotes the formation of vinegar, as these substances contain the requisite organic and inorganic food suited for the propagation of the vinegar fungus.

Vinegar with the help of Platinum Black. Dobereiner was the first who pointed out that, with the aid of platinum black, alcoholic vapours could be acetified in a very short time; and to this process the following apparatus is especially adapted. Fig. 248 shows a small glass house, in the interior of which are seen a number of compartments. The shelves forming these compartments support a number of porcelain capsules. The alcohol to be acetified is poured into these capsules, in each of which is placed a tripod, also of porcelain, supporting a watch-glass containing platinum black or spongy platinum. In the roof and at the bottom of the apparatus are ventilators, so constructed as to admit of regulating access of air. By means of a small steam pipe the interior of the house is heated to 33°. By this means the alcohol is gently evaporated, and coming into contact with the platinum black or sponge, is acetified. So long as the ventilation is maintained, the platinum black retains its property of oxidising the alcohol. With an apparatus of 40 cubic metres capacity and with 17 kilos. of platinum black, 150 litres of alcohol can daily be converted into pure vinegar. If it be desired to prepare the vinegar without any loss of alcohol, it becomes necessary to pass the outgoing air through a condenser in order to collect the vapours of alcohol and acetic acid which otherwise would be carried off.

FIG. 248.



Testing Vinegar. The value of a vinegar is dependent upon its flavour and upon its strength, or upon the quantity of acetic acid it contains. According to its containing more or less acetic acid the vinegar tastes more or less sour. The colour varies with the fluid from which the vinegar has been prepared; wine vinegar is of a yellow or red-yellow colour, fruit vinegar exhibits a golden colour, brandy vinegar is colourless; but as a rule the latter is coloured with caramel in imitation of wine vinegar. Freshly made vinegar contains besides small quantities of unconverted alcohol, some aldehyde, which always occurs largely in vinegar not properly prepared. Recently it has become customary to add a small quantity of glycerine to the prepared vinegar.

The quantity of acetic acid contained in a vinegar depends upon the alcoholic contents of the fluid to be acetified, and also upon the more or less perfect conversion of the alcohol into acetic acid. Malt vinegar contains from 2 to 5 per cent, brandy vinegar from 3 to 6 per cent, wine vinegar from 6 to 8 per cent, of acetic acid. The specific gravity of various kinds of vinegars differs from 1·010 to 1·030; the more alcohol a vinegar contains the lighter is it, the more extractive matter the heavier. The densities of mixtures of acetic acid ($C_2H_4O_2$) and water are, at 15° C., according to Oudemans, the following :—

Percentage.	Dens.	Diff.	Percentage.	Dens.	Diff.	Percentage.	Dens.	Diff.	Percentage.	Dens.	Diff.
0	0·9992	+15	26	1·0363	12	52	1·0631	7	78	1·0748	0
1	1·0007	15	27	1·0375	13	53	1·0638	8	79	1·0748	0
2	1·0022	15	28	1·0388	12	54	1·0646	7	80	1·0748	1
3	1·0037	15	29	1·0400	12	55	1·0653	7	81	1·0747	1
4	1·0052	15	30	1·0412	12	56	1·0660	6	82	1·0746	2
5	1·0067	16	31	1·0424	12	57	1·0666	7	83	1·0744	2
6	1·0083	15	32	1·0436	11	58	1·0673	6	84	1·0742	3
7	1·0098	15	33	1·0447	12	59	1·0679	6	85	1·0739	3
8	1·0113	14	34	1·0459	11	60	1·0685	6	86	10·736	5
9	1·0127	15	35	1·0470	11	61	1·0691	6	87	1·0731	5
10	1·0142	15	36	1·0481	11	62	1·0697	5	88	1·0726	6
11	1·0157	14	37	1·0492	10	63	1·0702	5	89	1·0720	7
12	1·0171	14	38	1·0502	11	64	1·0707	5	90	1·0713	8
13	1·0185	15	39	1·0513	10	65	1·0712	5	91	1·0705	9
14	1·0200	14	40	1·0523	10	66	1·0717	4	92	1·0696	10
15	1·0214	14	41	1·0533	10	67	1·0721	4	93	1·0686	12
16	1·0228	14	42	1·0543	9	68	1·0725	4	94	1·0674	14
17	1·0242	14	43	1·0552	10	69	1·0729	4	95	1·0660	16
18	1·0256	14	44	1·0562	9	70	1·0733	4	96	1·0644	19
19	1·0270	14	45	1·0571	9	71	1·0737	3	97	1·0625	21
20	1·0284	14	46	1·0580	9	72	1·0740	2	98	1·0604	24
21	1·0298	13	47	1·0589	9	73	1·0742	2	99	1·0580	27
22	1·0311	13	48	1·0598	9	74	1·0744	2	100	1·0553	
23	1·0324	13	49	1·0607	8	75	1·0746	1			
24	1·0337	13	50	1·0615	8	76	1·0747	1			
25	1·0350	13	51	1·0623	8	77	1·0748	0			

Acetometry. Commercial vinegar varies greatly as regards the quantity of acetic acid it contains. The specific gravity of a commercial vinegar is no certain indication of the quantity of acetic acid, owing to the fact that the vinegar nearly always contains foreign matters. The testing of the strength can therefore only be accurately effected by means of saturating it with an alkali. According to the ordinary method first introduced for this purpose by Otto, ammonia is added to the vinegar to be tested until the previously added tincture of litmus becomes again blue; although this method is not absolutely correct—owing to the fact that the neutral alkaline acetates exhibit an alkaline reaction—this does not much impair the correctness of this process. Otto's acetometer is a glass tube sealed at one end, 36 centims. long by 1·5 wide, whereon is engraved a double scale of divisions, one of these towards the bottom of the tube serving for measuring the vinegar coloured by litmus, while the other upper scale is intended for measuring the test liquor. When it is intended to apply the test with this measuring tube, a certain quantity (indicated by the divided scale) of litmus tincture is first poured into the tube, next vinegar is added in sufficient quantity to fill the tube up to the second division; afterwards so much of the test-liquor is added as to restore again the blue colour of the litmus.

The quantity of test-liquor employed indicates the percentage of acetic acid contained in the vinegar. The test-fluid should contain 1·369 per cent of ammonia. According to Mohr's method there are taken of the vinegar to be tested

$$\left(2C_2H_4O_2 - H_2O = \frac{102}{2} = 51\right);$$

and usually having a sp. gr. varying between 1·010 and 1·011, 5·04 c.c.,

$$\left(\text{for } \frac{5\cdot1}{1\cdot011} = 5\cdot04\right)$$

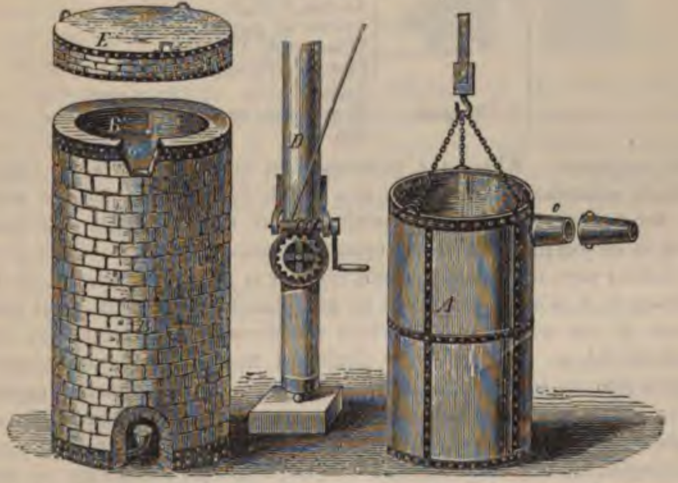
or simply 5 c.c., to which is added tincture of litmus, the whole being titrated with a normal alkali blue (a titrated caustic potassa solution rendered blue with litmus). It is better to take 10 c.c. of the vinegar and halve the number of c.c. of potassa employed.

Examples:—1. 10·0 c.c. of a Würtzburg table vinegar required
11·8 c.c. of potash solution, and the vinegar therefore contained
5·9 per cent of so-called anhydrous acid, or 6·7 per cent of acetic acid ($C_2H_4O_2$).
2. 10·0 c.c. of a vinegar prepared from wood vinegar required
12·5 c.c. of potash solution, corresponding to
6·25 per cent of anhydrous acid, or 7·3 per cent ($C_2H_4O_2$).

β. *Preparation of Vinegar from Wood Vinegar.*

Wood Vinegar. From the dry distillation of wood a portion of the carbonised matter remains in the retorts as charcoal, while the remainder of the constituents of the wood are eliminated partly in the state of gases and vapours, such as carbonic oxide, carbonic acid, hydrogen, light and heavy carburetted hydrogens—partly in the shape of a condensed matter, consisting of a thick, brown, oily fluid floating upon a stratum of a watery liquor. The latter, wood vinegar, consists essentially of impure acetic acid, some propionic and butyric acids, small quantities of oxyphenic acid, creosote, and an alcoholic wood spirit, a mixture of methylic alcohol, aceton, and acetate of methyl, the brown, thickish fluid substance known as wood tar, consisting of a number of both fluid and solid bodies, paraffin, naphthalin, creosote, benzol, toluol, &c. A well-conducted distillation will yield as much as from 7 to 8 per cent of the weight of the wood acetic acid. According to the researches of H. Vohl, peat can be employed in the preparation of wood vinegar and of wood spirit. 10 cwts. of peat yield 3 kilos. of acetic acid and 1·45 kilos. of wood spirit. The Table on the next page shows the principal products of the destructive distillation of wood.

FIG. 249.



Raw wood vinegar contains in solution a not inconsiderable quantity of resin, and also small quantities of phenol and guaiacol; all these bodies impart a more or less brown colour and empyreumatic odour and flavour, but they also render it a

- Wood
  - *a.* Wood
  - *b.* Hygroscopic Water
    - *α.* Illuminating Gas
      - Acetylen, C_2H_2
      - Elayl, C_2H_4
      - Trityl, C_3H_6
      - Ditretyl, C_4H_8
      - Benzol, C_6H_6
      - Toluol, C_7H_8
      - Xylol, C_8H_{10}
      - Naphthalin, $C_{10}H_8$
      - Carbonic oxide, CO
      - Carbonic acid, CO_2
      - Hydride of Methyl, CH_4
      - Hydrogen, H_2
    - *β.* Tar
      - Benzol, C_6H_6
      - Tolnol, C_7H_8
      - Styrolen, C_8H_8
      - Naphthalin, $C_{10}H_8$
      - Retene, $C_{18}H_{18}$
      - Paraffin, $C_{20}H_{42}$, or $C_{22}H_{46}$
      - Phenol
        - Carbolic acid, C_6H_6O
        - Cresylic acid, C_7H_8O
        - Phlorylic acid, $C_8H_{10}O$
      - Guaicol
        - Oxyphenic acid, $C_6H_6O_2$
        - Creosote — Combinations of oxyphenic acid and homologous acids with methyl*
          - $C_7H_8O_2$
          - $C_8H_{10}O_2$
          - $C_6H_{12}O_2$
      - Resin
    - *γ.* Wood Vinegar
      - Acetic acid, $C_2H_4O_2$
      - Propionic acid, $C_3H_6O_2$
      - Butyric acid, $C_4H_8O_2$
      - Valerianic acid, $C_9H_{10}O_2$
      - Caproic acid, $C_{10}H_{12}O_2$
      - Aceton, C_3H_6O
      - Acetate of methyl, $C_3H_6O_2$
      - Wood spirit, CH_4O
      - Phenol, Guaicol, and Resin
    - *δ.* Charcoal
      - Carbon .. .. 85 per cent.
      - Hygroscopic water 12 ,,
      - Ash .. .. .. 3 ,,

valuable antiseptic. Where the principal aim is to obtain wood vinegar, an iron retort, somewhat similar to a gas retort, is employed for the distillation of the wood; but in France, a vertical retort of boiler plate, exhibited at A, Fig. 249, is employed, fitted at the upper part with a tube, *o*, to which is fastened the projecting part, B. When the iron cylinder is filled with wood, a lid is tightly screwed on to it, it being next lifted up and placed into the cylindrical furnace, B, by means of the crane, D, after which the furnace is closed at the top with the firebrick lid, E. The products eliminated from the wood contained in the retort pass into the tube *b*, Fig. 250, and thence into the condensing apparatus, *c*, placed in a framework, *d*, which condensing apparatus is kept continually supplied with cold water by the tube *f*, while the warm water flows off at *k*. Vinegar, tar, and wood spirit are condensed and flow into the vessel *g*, in which the tar separates, the lighter fluids flowing into *h* through the tube *m*. The non-condensed gases pass through the tube *i* into the fireplace, where they assist in heating the retort, so that but very little fuel is required. In large factories, instead of the wooden receivers, large stone or brickwork cisterns are employed, generally several of such tanks being used, the largest quantity of tar being condensed in the first cistern, while the wood vinegar, mechanically freed from the tar and floating on its surface, finds its way into a second cistern. Pettenkofer's patent wood-gas generators produce a not inconsiderable quantity of wood vinegar.

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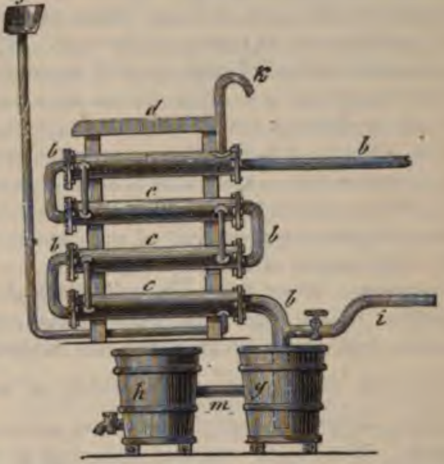
* According to S. Marasse (1868), Rhenish beech-wood tar creosote is a mixture of equal parts of—

Cresylic acid, C_7H_8O, boiling at 203°,
and Guaiacol · $C_7H_8O_2$,, 200°.

The latter is methylic ether with oxyphenic acid, $\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\}O_2$.

Purifying Wood Vinegar. Raw wood vinegar is a clear dark brown fluid, having a tarry taste and smoky odour. It is employed in small quantities in the preservation of meat, also for the preservation of wood, ropes, &c.; but by far the largest quantity is employed in the preparation of the various acetates used in dyeing and calico printing, chiefly as crude acetate of iron and crude acetate of alumina. It is also used in the preparation of concentrated acetic acid for industrial purposes, that is, for the preparation of aniline from nitro-benzol, and of sugar (acetate) of lead. Lastly, it is largely used in the preparation of table vinegar, an operation economical only where, as in England, there is a high duty on alcoholic fluids.

Fig. 250.



Among the means of purifying crude wood vinegar, the most simple—leaving out of the question the filtration of the crude liquor over coarsely granulated wood charcoal as recommended by E. Assmus—is distillation, an operation usually carried on in a still made of copper fitted with a copper condensing apparatus. At first a yellow fluid comes over—raw wood spirit from which the wood spirit of commerce is prepared—and next the distillate becomes richer in acetic acid.

The principal methods at present employed for the purification of wood vinegar may be considered as falling under either of two classes:—

α. The first includes the purifying of wood vinegar without saturation with a base; while

β. The second includes those methods in which the wood vinegar is purified by conversion into an acetate, the acetic acid being next separated by distillation with an acid possessing greater affinity for the base.

To the first class belongs Stoltze's method, consisting in first obtaining by distillation 10 per cent of a liquid which is employed for the preparation of wood spirit; 80 per cent of the liquid is next distilled off and the empyreumatic substances contained are destroyed by the action of either ozone or chlorine. The purification of the crude wood vinegar by the second method is more generally in use among manufacturers, the inventor of the system being Mollerat. The crude wood vinegar is first saturated with lime and the solution next precipitated with Glauber's salt to obtain acetate of soda; this salt is purified by crystallisation, and when in a dry state is so far heated that the empyreumatic matter it is mixed with becomes carbonised and is thus rendered insoluble; the acetate of soda is then extracted with water, and the acetic acid separated from it by distilling the previously crystallised and dried salt with sulphuric acid. Instead of acetate of soda the acetate of lime is frequently employed in the preparation of acetic acid from crude wood vinegar, the latter being saturated with lime, and the salt formed evaporated to dryness. The dry salt is roasted and treated similarly to the acetate of soda to calcine any empyreumatic products. The acid employed in the distillation is, according to the method invented by C. Völckel, hydrochloric acid. The distillation can be effected in a retort with a helm of copper and a condenser of lead, tin, or silver. Upon 100 parts of acetate of lime 90 to 95 parts of hydrochloric acid at 1·16 sp. gr. are used. When hydrochloric acid is used in this preparation instead of sulphuric acid, any contamination of the crude acetate of lime with empyreumatic or tarry matter does not affect the purity of the acetic acid which is obtained, provided the crude acetate be first so well dried as to be free from all other volatile substances; when sulphuric acid is used for this purpose the result is that an acetic acid is obtained, which contains not only a large quantity of sulphurous acid, but also other offensive volatile compounds due to the decomposition (by the sulphuric acid) of empyreumatic resins and tarry matter present in the crude acetate of lime.

Wood Spirit. When the acid liquid obtained by the dry distillation of wood is distilled on the large scale, there comes over at first a certain quantity of a yellow fluid, lighter than water, and exhibiting an ethereo-empyreumatic odour. This fluid (wood spirit) consists chiefly of methylic alcohol, CH_4O, or $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$, aceton, acetate of methyl, and other substances to which no reference need be made. Wood spirit was first discovered by Taylor in 1812, and was for a long time only employed for burning in spirit-lamps; it was not until 1822 that Taylor found this body was a new substance. Wood spirit is in a pure state a colourless fluid of 0·814 sp. gr., boiling at 66° C. It is in all respects very similar to alcohol, and can be employed as a source of heat in spirit-lamps; it evaporates, however, more rapidly and gives a less intense heat, for whereas 1 part by weight of alcohol yields by its complete combustion to carbonic acid and water 7189 units of heat, an equal quantity of wood spirit only yields 5307 units of heat. It is employed in the preparation of furniture polish and in varnish making; for these purposes, however, it requires to be well purified, and its rapid evaporation is a drawback to its extensive use; confirmed spirit drinkers have now and then used it instead of whiskey and the like, and, it appears, without bad effects. Its most recent use is in the preparation of iodide and bromide of methyl, which substances are employed in the manufacture of violet and blue coal-tar colours.

THE PRESERVATION OF WOOD.

On the Durability of Wood in general. The durability of wood, viz., its power of resisting the destructive influences of wind and weather, varies greatly, and depends as much upon the particular kind of wood and the influences to which it is exposed as upon the origin of the wood (timber), its age at the time of felling, and other conditions. Beech-wood and oak placed permanently under water may last for centuries. Alder wood lasts only a short time when in a dry situation, but when kept under water it is a very lasting and substantial wood. Taking into consideration the different kinds and varying properties of wood and the different uses to which it is applied, we have to consider as regards its durability the following particulars:—

1. Whether it is more liable to decay by exposure to open air or when placed in damp situations;

2. Whether it is when left dry more or less attacked by the ravages of insects which, while in a state of larvæ, live and thrive in and on wood.

Pure woody fibre by itself is only very slightly affected by the destructive influences of wind and weather. When we observe that wood decays, that decay arises from the presence of substances in the wood which are foreign to the woody fibre, but are present in the juices of the wood while growing, and consist chiefly of albuminous matter, which, when beginning to decay, also causes the destruction of the other constituents of the wood; but these changes occur in various kinds of wood only after a shorter or longer lapse of time; indeed, wood may in some instances last for several centuries and remain thoroughly sound; thus the roof of Westminster Hall was built about 1090. Since resinous woods resist the action of damp and moisture for a long time, they generally last a considerable time; next in respect of durability follow such kinds of wood as are very hard and compact, and contain at the same time some substance which—like tannic acid—to some extent counteracts decay. The behaviour of the several woods under water differs greatly. Some woods are after a time converted into a pulpy mass. Other kinds of wood, again, undergo no change at all while under water, as, for instance, oak, alder, and fir.

Insects chiefly attack dry wood only. Splint wood is more liable to such attack than hard wood; while splint of oak wood is rather readily attacked by insects, the hard wood (inner or fully developed wood) is seldom so affected. Elm, aspen, and all resinous woods are very seldom attacked by insects. Young wood, which is full of sap and left with the bark on, soon becomes quite worm-eaten, especially so the alder. birch, willow, and beech. The longer or shorter duration of wood depends more or less upon the following conditions:—

a. The conditions of growth. Wood from cold climates is generally more durable than that grown in warm climes. A poor soil produces as a rule a more durable and compact wood than does a soil rich in humus, and therefore containing also much moisture.

b. The conditions in which the wood is placed greatly influence its duration. The warmer and moister the climate the more rapidly decomposition sets in; while a dry, cold climate materially aids the preservation of wood.

c. The time of felling is of importance: wood cut down in winter is considered more durable than that felled in summer. In many countries the forest laws enjoin the felling of trees only between November 15 and February 15.

Wood employed for building purposes in the country, and not exposed to either heat or moisture, is only likely to suffer from the ravages of insects; but if it is placed so that no draught of fresh air can reach it to prevent accumulation of products of decomposition, decay soon sets in, and the decaying albuminous substances acting upon the fibre cause it to lose its tenacity and become a friable mass. Under the influence of moisture fungi are developed upon the surface of the wood. These fungi are severally known as the "house fungi" (*Thetephora domestica* and ***Boletus destructor***), the clinging fungus (*Cerulius vastator*). They spread over the wood in a manner very similar to the growth of common fungi on soil. Their growth is greatly aided by moisture and by exclusion of light and fresh air. A chemical means of preventing such growths is found in the application to the wood of acetate of oxide of iron, the acetate being prepared from wood vinegar. Wood is often more injuriously affected when exposed to sea water, when it is attacked by a peculiar kind of insect known as the bore-worm, *Teredo navalis*. This insect is armed with a horned beak capable of piercing the hardest wood to a depth of 36 centimetres. These insects originally belonged to and abound in great number in the seas under the tropical clime: but the *Teredo navalis* is met with on the coasts of Holland and England.

Preservation of Wood in Particular.

The means usually adopted to prevent the destruction of wood by decay are the following:—

1. The elimination, as much as possible, of the water from the wood previously to its being employed;

2. The elimination of the constituents of the sap;

3. By keeping up a good circulation of air near the wood so as to prevent its suffocation, as it is termed;

4. By chemical alteration of the constituents of the sap;

5. By the gradual mineralisation of the wood and thus the elimination of the organic matter.

Drying Wood.

1. Thoroughly dried wood remains for a long time unaltered while in a dry situation, more especially so when dried by so strong a heat that it becomes browned. When timber has to be put into a damp situation, it should, after having been well dried, be first coated with a suitable substance to prevent the moisture penetrating into the wood. This purpose is attained by coating the wood with linseed oil, so-called Stockholm tar, coal tar, creosote, and other hydrocarbons. Hutin and Boutigny adopt the following method to prevent the absorption of moisture by wood that is put into the ground. The portion of the post or wood to be buried is first immersed in a vessel containing benzol, petroleum, photogen, &c., and when taken out is ignited and thus charred. When extinguished the wood is put to a depth of from 3 to 6 centimetres into a mixture of pitch, tar, and asphalte, and next the entire piece of wood is thoroughly painted over with tar.

Elimination of the Constituents of the Sap.

2. The constituents of the sap are the chief cause of the decomposition of wood, and they should consequently be removed: many plans are adopted. In order that the wood may contain the smallest quantity of sap, it should be felled during the winter months. The constituents of the sap can be eliminated from the felled tree by three methods:—

a. By treatment with cold water, with which the wood must be thoroughly saturated to dissolve the constituents of the sap, which are removed when the wood is exposed to a stream of water. It is evident that with large timber a long time is necessary to ensure perfect saturation.

b. By employing boiling water the sap is removed much more quickly and efficiently. The pieces of wood are placed in an iron vessel with water and boiled. Large pieces of timber cannot be treated in this manner, but are immersed in a cistern in which the fluid is heated by means of steam. According to the thickness of the wood, the boiling occupies some 6 to 12 hours.

c. By treatment with steam (steaming of wood)—the most effectual method of removing the constituents of the sap, the hygroscopicity of the wood thus treated being rendered much less, while the wood is far more fitted to resist the effects of weather. The apparatus employed in carrying out the method consists of a boiler for the generation of steam, and a cistern or steam chamber, for the reception of the wood, this chamber being constructed of masonry and cement, of boiler plate, or being simply a large and very wide iron pipe. In most cases a jet of steam is conveyed from the boiler to the steam-chamber, where it penetrates the wood, and dissolves out the constituents of the sap, which on being condensed is allowed to run off. In the case of oak, this fluid is of a black-brown colour; with mahogany, a brown-red; with linden wood, a red-yellow; and with cherry tree wood, a red, &c. The operation is finished when the outflowing water is no more coloured. The steamed wood is dried in the air or in a drying room; it loses 5 to 10 per cent in weight by the process, and becomes of a much darker colour. The steam is sometimes worked at a temperature of above 100°, but generally the contents of the steam chamber are maintained at 60° to 70°. Towards the end of the operation some oil of coal-tar is introduced into the boiler, and is consequently carried over with the steam, impregnating the wood.

The removal of the sap can also be effected to some extent by means of mechanical pressure between a pair of iron rollers, which are gradually brought more closely together. Another method is by means of air pressure. Barlow employs for this purpose a metal case in which the wood is enclosed, and to one end of which an air pump is attached. Air being forced into the tube or case, the sap flows away at the end opposite to which the pump is attached. But both these methods are costly and not in all cases applicable.

Air Drains. 3. The construction of air drains or passages around woodwork to be preserved is, where the method is applicable, a great aid to the preservation of the wood. The consideration of the best means of effecting ventilation in this respect, is not a matter with which we can deal in this work. It is sufficient to say, that in many instances, the air channels are connected on the one hand with the open air, and on the other with the chimney.

Chemical Alteration of the Constituents of the Sap. 4. One of the most usual and most effective means of preventing the decomposition of wood is by effecting a chemical change in the constituents of the sap, so that fermentation can no longer be set up. To this class belongs the well-known plan of protecting woodwork that is to be exposed to the action of the moisture of the earth by charring the wood, either by fire or by treatment with concentrated sulphuric acid, so that the wood is coated to a certain depth with a layer of charcoal, the charcoal acting as an antiseptic. The charring or carbonisation of the wood can be effected either with the help of a gas flame or the flame from a coal fire. The apparatus of De Lapparent, invented for this purpose, became very generally employed in 1866 at the dockyards of Cherbourg, Pola, and Dantzic. According to another method the wood is impregnated throughout its whole mass with some substance that either enters into combination with the constituents of the sap, or so alters their properties as to prevent the setting up of decomposition. To this class belong the four following methods, these being the only ones that have met with any more extensive use.

1. Kyan's preserving fluid is a solution of bichloride of mercury of variable degree of concentration. In England a solution of 1 kilo. of corrosive sublimate in 80 to 100 litres of water is generally employed for railway sleepers. The timber is laid in a watertight wooden trough, containing the solution, where, according to its size, it remains a longer or shorter time. In Baden the wood remains in the kyanising solution, when it is to be impregnated to a depth of—

82 m.m.	for	4 days.
85 to 150	„	7 „
150 to 180	„	10 „
180 to 240	„	14 „
240 to 300	„	18 „

the solution consisting of 1 kilo. of sublimate to 200 litres of water. The prepared wood is washed with water, rubbed dry, and then placed in sheds free from exposure to rain and strong sunlight. The principal action of the bichloride of mercury is to convert the albumen of the sap into an insoluble combination, capable of withstanding decomposition, while the bichloride becomes gradually reduced to protochloride of mercury (calomel). A great objection to this method is the danger to which the carpenter or joiner who may afterwards shape the wood is exposed, the free chemicals acting upon his system through his hands, nostrils, and mouth. In England wood to be varnished is seldom kyanised.

Erdmann remarks upon this plan of preserving wood that the interior of the log is still left in its original condition. To answer the objection the kyanising has been made more effective by placing the wood into a water-tight trough, with the solution of sublimate, and by a great pressure of air thoroughly impregnating the wood. Kyanising by this method becomes, however, as expensive as any other impregnation method. Recently there has been substituted for the pure bichloride of mercury a double salt of the formula $HgCl_2+KCl$, obtained by decomposing a solution of carnallite with oxide of mercury.

2. Burnett's patent (1840) fluid consists of 1 kilo. of chloride of zinc dissolved in 90 litres of water. Wood treated with Burnett's fluid has been buried in earth for five years without undergoing any change, while unprepared wood buried for the same length of time has been totally destroyed. Chloride of zinc has been much used in Germany as an impregnating material. Besides this salt sulphate of copper and acetate of oxide of zinc—pyrolignite of zinc (Scheden's method), have been employed. The action of the copper and zinc salts may be explained by considering that the metallic oxides of the basic salt formed during seasoning, separates and combines with the colouring matter, tannic acid, resin, &c. of the wood, to form an insoluble compound.

3. Bethell's (1838) patented method consists in treatment under strong pressure with a mixture of tar, oil of tar, and carbolic acid, this mixture being known commercially by the name of *gallotin*. In and near London wood thus treated has remained eleven years in the earth without undergoing change; other pieces of timber so treated were subjected to the action of the sea for four years and still were in good condition. Vohl employs for preservation peat and brown coal creosote; Leuchs uses paraffin. Such agents, however, render wood treated with them highly inflammable.

4. Payne's method. This includes two patents, the first having been taken out in 1841. Both are based on the impregnation of the wood—first with one salt, and next with another salt, which is capable of forming a precipitate insoluble in water and sap of the wood with the first. The first solution is usually one of sulphate of iron or of alum, then follows a solution of chloride of calcium or of soda. The wood to be impregnated is placed in a vessel from which the air is exhausted, the first solution being then admitted, and subsequently pressure is applied. The first solution being removed, the second is admitted, and pressure again applied. It is necessary to dry the wood partially between the two impregnations. Payne's method, much used in England, possesses, moreover, the advantage of rendering the wood somewhat uninflammable. The same effect results with the methods of Buchner and Von Eichthal, who impregnate the wood with a solution of sulphate of iron, and then with a water-glass solution, whereby the pores of the wood are filled with ferro-silicate. Ransome attains the same end by an impregnation with a water-glass solution and subsequent treatment with an acid. It is found that the treatment of wood according to the above methods is generally attended with good results. A method of impregnation with materials forming an insoluble soap, oleate of alumina, oleate of copper, &c., patented in 1862, has given some moderate results on the small scale.

Mineralising Wood. 5. When the terms mineralised, petrified, metallised, or incrusted are applied to wood, they include the meaning that the wood has undergone impregnation with an inorganic substance, which has so filled the pores of the wood that it may be said to partake of the characteristics of a mineral substance. Suppose that the wood has become impregnated with sulphate of iron, when exposed to the rain the sulphate will be gradually dissolved out, in time leaving only a basic sulphate. By the researches of Strützki (1834), of Apelt in Jena, and of Kuhlmann (1859), the influence of oxide of iron upon wood fibre has been rendered very clear. Wood impregnated with basic sulphate of iron ceases to be wood after some time.

Boucherie's Method of Impregnation.

6. This method consists in the impregnation of the wood with the necessary substance, in a manner similar to the natural filling of the pores with sap; that is to say, the solution is introduced into the tree from its roots, and is thus made to take the place of the sap in all parts of the timber. When the tree is felled the root end is placed in a solution of the salt (sulphate of copper, acetate of iron), and allowed to remain for some days; at the end of the required time the wood will have become completely impregnated with the salt. Occasionally this method is employed in colouring woods, colouring matter being used instead of, or as well as, the salt. The linden, beech, willow, elm, alder, and pear tree can be treated in this manner. The fir, oak, ash, poplar, and cherry tree do not, however, absorb the impregnating fluid sufficiently.

TOBACCO.

Tobacco.

Tobacco, as employed for snuff and for smoking and chewing, is the product of various kinds of annual plants belonging to the genus *Nicotiana*, of the family of *Solanea*, generally cultivated in warmer parts of the globe, but capable of growing in countries situated under 52° N. lat. The best tobaccos are grown in America, and are chiefly exported from the southern states of North America, viz., Maryland, Virginia, &c., from Orinoko, Havanna, and Cuba, &c. The European tobaccos are those of Holland, Hungary, Turkey, and France. In Europe three separate botanic varieties are cultivated. They are:—

1. Common or Virginian tobacco (*Nicotiana tabacum*), with a large lancet-shaped ribbed leaf.
2. Maryland tobacco (*Nicotiana macrophylla*), with broad and not so strongly pointed leaves as those of the common tobacco plant.
3. The farm or violet skin tobacco (*Nicotiana rustica*), with an oval leaf and long stalk.

The quality of the tobacco is dependent upon the climate, upon the soil, and upon the seed it is obtained from. Next to the vine, the tobacco plant is that requiring the most care in its cultivation. The influence of careful culture is so great, that plants grown in some parts of Germany yield tobacco unequalled by some of the richest tropical produce.

According to the most recent researches, tobacco contains the following substances:—

Mineral bases	Potash Lime Magnesia Oxides of iron and manganese Ammonia	Organic base	Nicotine
Mineral acids	Nitric acid Hydrochloric acid Sulphuric acid Phosphoric acid	Organic acids	Malic acid (Tobacco acid?) Citric acid Acetic acid Oxalic acid Pectic acid Ulmic acid

Other mineral substances	Silica Sand	Other organic substances	Nicotianin Green and yellow resin Wax or fat Nitrogenous substances Cellulose

Chemical Composition of the Tobacco Leaf. The chief characteristic constituents of the tobacco leaf are the three following:—namely, nicotianin, nicotine, and malic acid. Nicotianin, or tobacco camphor, is a fatty substance, possessing strongly the odour of tobacco, and a bitter, aromatic flavour. Experience has shown that the varieties of tobacco containing the most nicotianin are those most preferred. It is generally considered that nicotianin is identical with cumarin ($C_9H_8O_2$), found in the tonka bean (*Dipterix odorata*), in the *Asperula odorata*, in the *Melilotus officinalis*, and *Anthroxanthum odoratum*, as well as in the leaves of the *Angraecum fragrans*, and the *Liastris odoratissima*. Nicotine ($C_{10}H_{14}N_2$) is an organic base, and exists in a pure condition as a colourless oil, possessing the odour of tobacco and a caustic flavour; it is soluble in water, alcohol, ether, and some oils. It is even in very small doses a deadly poison; and in the very smallest quantities it will cause convulsions and paralysis. The proportion of nicotine met with in the various kinds of tobacco leaves varies greatly. From the experiments of Schlœsing, made with many kinds of French and American tobaccos, the following quantity per cent of nicotine is found in the dry leaves of tobacco from:—

	Nicotine.
Departement Lot	7·96
„ Lot-et-Garonne	7·34
„ Nord	6·58
„ Ille-et-Villaine	6·29
Pas de Calais	4·94
Alsace	3·21
Virginia	6·87
Kentucky	6·09
Maryland	2·29
Havanna ... ... less than	2·00

Dried snuff-tobacco contains about 2 per cent of nicotine, and contains on an average in its undried (usual) condition 33 per cent of water, the nicotine then amounting to 1·36 per cent. The nicotine is contained in the tobacco in the form of a salt. The characteristic acid is nicotic or tobacco acid, $C_3H_4O_4$, which recent numerous researches have proved to be identical with malic acid. The tobacco leaf also contains albumen, woody fibre, gums, and resin. The leaves are also very rich in mineral constituents, these amounting to 19 to 27 per cent of the weight of the dried leaf. Merz obtained about 23·33 per cent ash with several varieties of tobacco leaf. 100 parts of this ash contained potash, 26·96; soda, 2·76; lime, 39·53; magnesia, 9·61; chloride of sodium, 9·65; sulphuric acid, 2·78; silica, 4·51; and phosphate of iron, 4·20 parts. There is found, also, nitrate of potash, the quantity of which does not, however, influence the combustibility of the tobacco.

Manufacture of Tobacco. Good smoking tobacco should give off an agreeable odour, should not deflagrate while burning, and not bite the tongue. Taste differs considerably in the respect of strength in this country from abroad; nowhere but in the

United Kingdom are such strong smoking tobaccos met with. The freshly dried tobacco leaves are not suited for smoking, because they contain a very considerable amount of albuminous matter, and on burning give off an odour of burnt horn, while they contain too large a quantity of nicotine. The preparation or manufacture of tobacco aims at the more or less complete destruction of the albuminous matters, the partial elimination of the nicotine, and the development of a peculiar aroma, while the leaves are formed by mechanical means into a suitable shape for smoking and snuffing. The leaves are moistened with water and placed together in heaps so as to cause a kind of fermentation, the temperature increasing to about 35°, the effect of which is that the albuminous matter of the tobacco is destroyed, while aromatic substances are developed. This process is assisted by the addition of what the trade terms "sauce," but nothing is known of the reactions and changes which take place. When the tobacco leaves are gathered from the plants they are laid one upon the other to the number of ten or twelve and placed in heaps in a dry shed, care being taken to cover the heaps with canvas. As soon as the sweating sets in, the leaves are suspended one by one on ropes stretched through the shed, and dried by exposure to a current of air; when dry the leaves are packed together to the number of thirty, so as to form a bundle, several hundreds of which are put together into casks. The weight of the casks filled with tobacco averages from 19 to 26 cwts. In some, but by no means in all instances, the cultivators of tobacco prepare the leaves to some extent by first moistening them with brine and causing them to undergo a partial fermentation. The leaves are then dried and packed in casks. By this means the tobacco may be preserved for a great many years, improving with age.

Smoking Tobacco. The tobacco leaves are first sorted; that is, those of the same colour and thickness are put together. They are next stripped, the thicker parts (stem or nerve) being cut out, because as these consist chiefly of woody fibre they would on burning impart an unpleasant odour to the tobacco. The leaves are next sauced or moistened with a liquor containing chiefly salts (common salt, saltpetre, sal-ammoniac, nitrate of ammonia), saccharine matter, spirits, and some organic acids, such as tartaric and oxalic acid; the salts assist in the preservation as well as in the retardation of the combustion of the tobacco. The other substances impart, under the influence of fermentation, a peculiar aroma to the tobacco, which aroma is sometimes compared to the bouquet of wine. The sauced leaves are next submitted to fermentation, dried at a gentle heat, and finally cut into shreds by means of machinery. Tobacco leaves are also twisted or spun together; for instance, in the kind known as twist. Cigars are tobacco enveloped in a smooth leaf. The fact that cigars are improved by keeping is due to a kind of slow fermentation, during which the aroma is more fully developed, while noxious substances are eliminated.

Tobacco smoke contains, in addition to carbonic acid, water, and some ammonia, the products of the dry distillation of tobacco, to which the peculiar flavour is due—among these substances are nicotine and nicotianin. Zeise found in tobacco smoke a peculiar empyrematical oil, butyric acid, ammonia, carbonic acid, paraffin, empyreumatic resin, traces of acetic acid, oxide of carbon, and carburetted hydrogen.

Curiously enough, burning tobacco does not form carbolic acid nor creosote; hence tobacco smoke affects the eyes less than does the smoke of smouldering wood. Zeise experimented on Porto Rico tobacco; but his researches fail to convey any information as to the constitution of the essential aroma of tobacco smoke; in this respect it is with tobacco as with the bouquet of fine brands of wine, chemical reagents cannot detect the difference. But it is certain that tobacco smoke contains conjugated ammonias, and as aniline has, in very dilute state, a similarity in odour with the smoke of good tobacco, it may be present. Carbolic acid may also be produced by the dry distillation of tobacco. The combustibility of tobacco is not proportional to the quantity of nitric acid (nitrates) it contains, because while Kentucky tobacco, rich in nitrates burns badly, the Java, Maryland, Brazilian, and Hungarian tobaccos, poor in nitrates, burn readily. Schlœsing has recently investigated the cause of the varying degree of the combustibility of tobacco. He found that the portion of tobacco ash soluble in water always contains carbonate of potash in proportion to the combustibility of the weed. When tobacco was carbonised by smoking, the soluble portion of the ash was found to contain only chloride of potassium and sulphate of potash. A badly burning tobacco is improved by saucing it with the solution of a potash salt of some organic acid (malic, citric, tartaric, or oxalic acid), and then drying the tobacco; on the other hand, a good burning tobacco is deteriorated by treating it with solutions of either sulphate of lime, chloride of calcium, or the corresponding magnesia and ammonia compounds. The cause of this phenomenon appears to be due to the fact that the potash salts of the organic acids yield on being carbonised a bulky, light, and very porous charcoal, which readily burns off, leaving only ash, while the charcoal formed by the combustion, under the same conditions, of the organic lime salts is very compact, hard, and burning off with difficulty.

Snuff. For the making of snuff the tobacco leaves are sorted as for smoking tobacco, but the sauce is chiefly composed of ammoniacal salts and aromatic substances. The fermented leaves are formed into *carottes*, thick beet-root shaped masses tapering from the centre to both ends, but not drawn out into a thin spindle; these carottes are rasped (*rappé*) by means of machinery, and thus converted into powder. After having been sifted, this powder is again moistened and submitted to another fermentation. Snuff contains nicotine, partly free, partly as a neutral or basic (probably acetate) salt to an amount of about 2 per cent. Snuff also contains ammonia combined with an acid. It is to the presence of these substances that snuff owes its irritating action on the mucous membrane. In order to prevent snuff from becoming dry glycerine is frequently added.

The aim of the fermentation of the tobacco for the purpose of snuff making appears to be :—1. The formation of a peculiar oil or ether which imparts aroma. 2. The partial destruction of the nicotine of the tobacco so as to render it better fitted for use as snuff. 3. The production of alkalinity by the partial destruction of the organic acids of the tobacco. 4. Evolution of a specific flavour by the formation of vapours of carbonate of ammonia (probably also of ammonia bases, such as ethylamin), and nicotine. 5. The conversion of the albuminous matters and other nitrogenous substances into ammonia, whereby the loss of ammonia by volatilisation is made up and a black substance (humus), to which snuff owes its dark colour, at the same time formed.

TECHNOLOGY OF ESSENTIAL OILS AND RESINS.

Essential Oils and Resins. These substances almost all occur naturally. To the essential oils most plants owe their odour and flowers their perfume. The essential oil in plants is met with enclosed in cells; hence, after bruising a plant, or the parts containing the essential oil, the peculiar odour is more perceptible; for instance, by gently rubbing between the fingers the leaves of some kinds of geraniums, melissa, lemon-plant, &c. Essential oils do not impart to the fingers a fatty, but a rather rough, harsh feeling. A large number of essential oils possess the property of precipitating silver from its ammoniacal solution in a metallic state; hence the use of essential oils in silvering glass (See p. 281).

Preparation of Essential Oils. These oils are chiefly obtained by submitting parts of plants, previously ground to a coarse powder, to distillation with water. Although the boiling-point of these oils is generally much higher than that of water, the oils are mechanically carried over in a minute state of division with the aqueous vapour. When oils, the boiling-point of which is very high, have to be extracted, some common salt is added to the water to heighten its boiling-point. In order to separate the oil from the water there is employed a peculiarly shaped vessel called a Florentine flask. In this way the essential oils of aniseed, chamomile, lavender, peppermint, cloves, cinnamon, &c., are obtained, while the most common essential oil, viz., that of turpentine, is obtained by the distillation of Venice turpentine with water.

Preparation of Essential Oils by Pressure. The essential oils largely met with enclosed in the cells of the skin of lemons, oranges, bergamots, and, in fact, all the fruits belonging to the *Citrus* species, are obtained by pressing the rind of these fruits. Although the greater number of the essential oils occur ready formed in various parts of the plants, some of these oils are the result of the action of water, as, for instance, the essential oil of bitter almonds, which is formed by the action of water upon amygdalin under the influence of a pecular albuminous compound called synaptase or emulsin; the essential oil of mustard seed is formed in a similar manner, but may be artificially prepared by distilling a mixture of iodide of propyl and cyanide of potassium, &c.

Extraction of Essential Oils by means of Fatty Oils. Some of the essential oils, more especially those present in flowers, are so sparingly distributed that they can only be obtained by digesting the fresh flowers with pure olive oil or with cotton-wool soaked in sweet olive oil, the fresh flowers being placed in alternate layers between the cotton saturated with oil; in some cases pure lard is employed. The essential oils may be recovered from the sweet oil by agitation with strong and highly rectified alcohol. The essential oils of jasmine, sweet violets, hyacinths, &c., are obtained in this manner.

Properties and Uses of Essential Oils. These oils are more or less soluble in water, and the solutions are known in pharmacy as distilled waters. The essential oils are soluble in alcohol in proportion to the amount of oxygen they contain. Upon this property is based the use of these oils in perfumery and for the preparation of liqueurs (cordials).

Perfumery. This branch of industry provides us with scented waters (*esprits eaux de senteur*), odoriferous extracts (*extraits à odeurs*), perfumed fats, pomatums, oils, &c. Scented waters are really alcoholic solutions of one or more essential oils. The alcohol used for this purpose requires to be very pure and perfectly free from fusel oil or other impurity. The oils are dissolved in the alcohol, and in order to blend the mixture and render it mellow, it is kept for several months in a bottle before being sold. The old process of distillation is very properly discarded, because, owing to the high boiling-point of the oils, a portion was left in the still, while the scented waters thus prepared were inferior in quality. *Eau de Mille Fleurs* is prepared by dissolving in 9 litres of alcohol, 60 grms. of balsam of Peru, 120 grms. of oil of bergamot, 60 grms. of oil of cloves, 15 grms. of neroli oil (oil of orange flowers, a very expensive oil), 15 grms. of oil of thyme, adding to the mixture 4 litres of orange-blossom water, 120 grms. of tincture of musk, obtained by digesting 15 grms. of civet and 75 grms. of musk with 2 litres of alcohol. *Eau* *de Cologne* is obtained by dissolving in 6 litres of alcohol 32 grms. of essential oil of orange-peel and equal quantities of oil of bergamot, lemon, *essence de limette*, *essence de petit grains*, 16 grms. *essence de cedro*, and equal quantities of *essence de cedrat*, *essence de Portugal;* further, 8 grms. of neroli oil and 4 grms. of rosemary.

The perfumed extracts are generally obtained by the exhaustion, by means of alcohol, of the scented fats and oils prepared from flowers as before described. Doebereiner first suggested the use of artificial perfumes; among these are an

Chemical Perfumes.

alcoholic solution of acetate of amyl as pear oil, valerate of amyl as apple oil, buterate of amyl as pine-apple oil, pelargonate of ethyl as oil of quinces, suberate of ethyl as essence of mulberries, while nitrobenzol mixed with nitrotoluol (commercial nitrobenzol) is termed artificial oil of almonds, and, when very coarse, is sold as *essence de Mirbane*, chiefly used for the preparation of aniline. The perfumed fats (pomatums) of better quality are generally prepared from an infusion of the flowers with oil or fat at a temperature of 65°, or by a process of digestion in the cold by placing the flowers in layers between pure lard or cotton-wool soaked in very pure olive oil; *enfleurage* is the name given to this operation. The ordinary pomatums are made simply of lard or marrow-fat coloured with turmeric, annatto, or alkanet root, and perfumed with a few drops of some essential oil.

Preparation of Cordials.

The aim of the preparation of liqueurs (cordials) is to render brandy a more agreeable beverage by the addition of sugar, glycerine, and aromatic substances. A distinction is made between finer liqueurs (*rosoglio*) and ordinary cordials (*aqua vitæ*) according to the quality of the materials employed for the purpose. When a sufficiently large quantity of sugar is used to render the liqueurs thickly fluid they are designated crèmes, while those made with the juices of fruit obtained by pressure, sugar, and alcohol, are called ratafia. These liqueurs are not prepared to any great extent in this country; but in France, Italy, Austria, and especially Holland, the preparation is on a large scale.

The basis of all liqueurs is a very highly rectified and pure alcohol. The vegetable materials used in the liqueurs may be classified under three heads:—In the first place, such vegetable substances as contain essential oils and are used for that reason only, carraway, aniseed, juniper-berries, mint, lemon-peel, orange-blossom, and bitter almonds. These substances, previously bruised or cut up, are digested with alcohol, the mixture being next distilled, or, as is more generally the case, alcoholic solutions of the essential oils are employed and the preparation performed in the cold. To the second class belong such vegetable substances as are used for the sake of their essential oil and for their aromatic bitter substances, chiefly roots, such as sweet calamus, gentian, ginger, orange-peel, unripe bitter Curaçoa apples (a peculiar kind of orange), wormwood, cloves, cinnamon, vanilla (the pod of an orchidaceous plant originally brought from Mexico). These substances having been bruised are digested with alcohol either at the ordinary temperature of the air or at 50° to 60°, the result being the formation of what is termed a tincture. To the third class belong fruits, such as cherries, pine-apples, strawberries, raspberries, the juice of which is obtained by pressure, passed through a sieve, and mixed with alcohol and sugar or syrup, viz., a solution of 4 lbs. of refined loaf-sugar in 4 litres of water. The liqueurs generally contain from 46 to 50 per cent of alcohol. It is customary to colour the liqueurs red with santal-wood, cochineal, aniline red, or with the *Coccus polonicus*, as is the case with the celebrated Alkermes de Firense.

a liqueur made at Florence; yellow with saffron, turmeric, or marigold flowers (*Calendula*); green by mixing yellow and blue; blue with tincture of indigo; violet with aniline violet; while in many cases caramel is used to impart a brown colour. The so-called *crêmes* contain for every litre of liquid about 1 lb. of sugar or a corresponding quantity of glycerine. As an instance of the composition of a liqueur, Maraschino consists of 4 litres of raspberry water, 1¾ litres orange-blossom water, 1½ litres kirschwasser (a Swiss preparation—from cherries fermented and distilled—a strong spirituous liquid which contains hydrocyanic acid), 18 lbs. of sugar, and 9 litres of alcohol at 89 to 90 per cent. Liqueurs are very similar to *crêmes*, but contains less sugar. English bitter contains 5 parts of *flavedo corticum aurantiorum* (outer rind of dried orange peel), 6 parts of cinchona bark, 6 parts of gentian, 8 parts of *Carduus benedict*, 8 parts of centaury, 8 parts of wormwood, 4 of orris root digested with 54 litres of alcohol at 50 per cent, while after filtration 12 lbs. of sugar are added. Cherry ratafia:—20 litres of cherry juice, 20 litres of alcohol at 85 per cent, 30 lbs. sugar, and usually 4 to 8 litres of bitter almond water. Peppermint:—2½ litres of essential oil of peppermint dissolved in 1 litre of alcohol at 80 per cent; this solution is poured into 54 litres of alcohol at 72 per cent sweetened with 60 lbs. of sugar previously dissolved in 26 litres of water, and coloured with either tincture of indigo or turmeric.

Resins. By the action of the oxygen of the air most of the essential oils are gradually thickened, and at length converted into a substance termed resin. Resins are frequently met with in the vegetable kingdom; in some instances, as with coniferous trees, resin flows spontaneously from the wood in combination with an essential oil, so-called Venice turpentine, which hardens by exposure to air. Some resins are extracted from vegetable matter by means of alcohol, this solution being either precipitated with water or evaporated to dryness. Resins are either soft, and are then termed balsams, chiefly solutions of resin in essential oils, or hard. To the former belong Venice turpentine, Canada balsam, balsam of Peru, Copaiva balsam, &c.; to the latter, amber (a fossil resin), anime, copal, gum dammar, mastic, shellac, asphalte. The gum resins are obtained from incisions made in certain kinds of plants, the milky juice of which hardens by exposure to air; these substances are partly soluble in water, and yield with it in many instances an emulsion; for instance, assafœtida, gum gutti, &c. Many gum resins possess a very strong odour and contain essential oils. Although it is customary to treat of caoutchouc and gutta-percha under the head of resins, these substances are not related to resins at all, but belong to a separate class of bodies, among which, according to Dr. G. J. Mulder's researches, the so-called drying oils must be enumerated.

Use of Resin as Sealing-Wax. Sealing-wax of modern time (for mediæval sealing-wax was really a mixture of wax with Venice turpentine and colouring matter) is prepared from shellac, to which some turpentine is added in order to promote fusibility and prevent brittleness. Red sealing-wax and bright coloured wax are made of a very pale, sometimes even purposely bleached, shellac, while black and dark coloured sealing-wax are made of more deeply coloured shellac. In addition to shellac and turpentine, sealing-wax contains earthy matter, added not only for the purpose of increasing the weight, but also for preventing the too rapid fusion of the mass; chalk, magnesia, plaster of Paris, zinc-white, sulphate of baryta, kaolin, finely-divided silica, are employed for this purpose. Red sealing-wax is prepared by melting together in an iron pan placed on a charcoal fire 4 parts of shellac, 1 part of Venice turpentine, and 3 parts of cinnabar (vermillion), care being taken to stir the mixture constantly. Ordinary red sealing-wax is often composed of:—

	1.	2.	3.	4.	5.
Shellac	550	620	550	700	600
Turpentine	740	680	600	540	600
Chalk or magnesia	300	200	—	—	—
Gypsum or zinc-white	200	—	—	—	—
Baryta white	—	100	380	300	300
Vermillion	130	220	340	300	300
Oil of turpentine	—	—	—	20	25

The cooled but still soft mass is either rolled on a slab of marble and shaped into sticks, or the fluid mass is run into brass moulds. Perfumed sealing-wax contains either benzoin resin, storax, or balsam of Peru. The various colours are imparted by cobalt ultramarine (cobalt blue), chromate of lead, bone-black, &c. Marbled sealing-wax is made by mixing variously coloured sealing-wax together. Inferior kinds of sealing-wax—parcel-wax—are coloured with red oxide of iron, while instead of shellac ordinary resin is used with gypsum or chalk. New Zealand resin, the produce of the *Xanthorrhœa hastilis*, is now frequently used instead of shellac.

Asphalte. This material sometimes known as bitumen, is a black, glossy, brittle resin, probably formed by the gradual oxidation of petroleum oil; it occurs very largely on the island of Trinidad, on the northern coast of S. America, at the mouth of the Orinoco, on the water of the Dead Sea (anciently *Lacus Asphaltites*), and in some other localties, viz. France, Seyssel, Departement de l'Ain, a limestone containing 18 per cent of asphalt. By boiling this limestone, previously broken up into small lumps, with water, there is obtained an asphalte, 7 parts of which are mixed with 90 parts of native asphalte limestone. The materials are ground up together and are employed for paving purposes, being compressed with heavy and highly heated irons. Asphalte also occurs at Val de Travers, Switzerland; Limmer, Hanover; Lobsann, Lower Alsace; and in the Northern Tyrol. Asphalte, or bitumen, is somewhat soluble in alcohol, readily so in Persian naphtha, oil of turpentine, benzol, and benzoline. It is used in varnish making (iron varnish), in engraving copper and steel, as an etching ground, and as an oil paint. Asphalte mixed with sand, lime, or limestone, is largely used for paving purposes, being durable and somewhat elastic; it is employed for this purpose either in a pasty or semi-fused state, or in powder. Instead of native asphalte, Busse's terresin, a mixture of coal-tar, lime, and sulphur is sometimes used, as well as coal-tar asphalte, obtained from gas works. The residue of the distillation of coal-tar is often employed instead of asphalte, and pebbles mingled with coal-tar are now used to form excellent footpaths in some parts of the metropolis.

Caoutchouc. Elastic gum or india-rubber, is derived from the the milky juice of a series of plants, occurring also in opium; but the commercial article is obtained from the milky juice of various trees belonging to the natural orders of the *Urticeæ*, *Euphorbiaceæ*, *Apocyneæ*. Among the trees which yield caoutchouc in large quantity are the *Siphonia cahucu*, in South America, and the East Indian, *Urceola elastica*. *Ficus elastica*, *F. religiosa*, *F. indica*, also yield caoutchouc. It is obtained by making incisions in the tree and collecting the exuding juice in vessels of dried clay

The juice is solidified by the application of fire or by exposure to the sun's rays; the variety known as lard gum is usually dried by exposure to the sun. Perfectly pure caoutchouc is a white, and in thin sheets semi-transparent, substance; its texture is not fibrous; it is perfectly elastic, becoming turbid and fibrous when strongly stretched. Excessive cold renders it hard but not brittle. The specific gravity of caoutchouc is 0·925. Although hot water and steam render caoutchouc soft, it is not further acted upon by them. It is insoluble in alcohol, not acted upon by dilute acids or strong alkalies, while for a very long time it resists the action of chlorine. Strong sulphuric and nitric acids decompose india-rubber, and when red fuming nitric acid is employed a violent combustion ensues. If when strongly stretched india-rubber is placed in cold water for a few minutes it temporarily loses its elasticity, which it regains by being immersed for a few minutes in water at 45°. By exposure to a gentle heat caoutchouc becomes supple, and finally melts at 200°, with partial decomposition, forming a viscous mass which does not again become solid on cooling. When caoutchouc is ignited in contact with air it burns with a sooty flame. Of all substances with which we are acquainted none would be better suited to gas manufacture than caoutchouc, which, according to experiments made many years ago at Utrecht, yields at red heat rather more than 30,000 cubic feet of gas to the ton, the gas being quite free from sulphur and ammonia compounds, and its illuminating power very superior to that of the best oil gas. Unfortunately caoutchouc is much too high priced for this application. Caoutchouc may be kneaded with sulphur and other substances by the aid of heat, becoming converted into what is known as vulcanised india-rubber, vulcanite, ebonite, &c. When caoutchouc is submitted to dry distillation, at much below red heat, it yields only oily fluids, consisting of carbon and hydrogen (caoutchen, heveen, &c.), which are *par excellence* solvents for caoutchouc. Caoutchouc itself contains only carbon and hydrogen, its formula being C_4H_7 (in 100 parts: 87·5 carbon and 12·5 hydrogen); probably, however, caoutchouc is a more complex mixture of various hydrocarbons.

Solvents of Caoutchouc. India-rubber is soluble in alcohol-free ether, in the oils (empyreumatic) of caoutchouc, in Persian naphtha, oil of turpentine, sulphide of carbon, and in chloroform. Industrially the ethereal solution of caoutchouc is useless, because it contains hardly more than a trace of that substance. As regards oil of turpentine, it dissolves caoutchouc only when the oil is very pure and with the application of heat; the ordinary oil of turpentine of commerce causes india-rubber to swell rather than to become dissolved. In order to prevent the viscosity of the india-rubber when evaporated from this solution, 1 part of caoutchouc is worked up with 11 parts of turpentine into a thin paste, to which is added ¼ part of a hot and concentrated solution of sulphuret of potassium (K_2S_5) in water; the yellow liquid formed leaves the caoutchouc perfectly elastic and without any viscosity. The solutions of caoutchouc in coal-tar naphtha and benzoline are most suited to unite pieces of caoutchouc, but the odour of the solvents is perceptible for a long time. As chloroform is too expensive for common use, sulphide of carbon is the most usual and also the best solvent for caoutchouc. This solution, owing to the volatility of the menstruum, soon dries, leaving the caoutchouc in its natural state. When alcohol is mixed with sulphide of carbon the latter does not any longer dissolve the caoutchouc, but simply softens it and renders it capable of being more readily vulcanised. Alcohol precipitates solutions of caoutchouc and gutta-percha.

Preparation and Use of India-Rubber. India-rubber is used to clean paper, rub out black-lead pencil marks, for making waterproof fabrics (macintosh), rubber sponge, tubing, elastic webs, lutes, &c.

Vulcanised Caoutchouc. When caoutchouc is immersed for some time in molten sulphur it absorbs the latter, and becomes converted into a yellow, very elastic mass. The properties of vulcanised india-rubber are: elasticity even at low temperatures, while ordinary india-rubber hardens at 3°. Vulcanised india-rubber is insoluble in the solvents of caoutchouc. It resists compression to a very great extent; hence its use instead of steel springs on the tramway cars. According to the old method caoutchouc was vulcanised by being placed for some ten to fifteen minutes in thin plates in molten sulphur heated to 120°, the weight of the caoutchouc increasing 10 to 15 per cent. The material was subsequently mechanically treated by pressure, and then heated to 150°. In order to prevent efflorescence of the sulphur, caoutchouc is sometimes heated to 120°, and then kneaded, by the aid of powerful machinery, with either kermes (Sb_2S_3), or a mixture of sulphur and sulphuret of arsenic. At the present day Parkes's method is generally adopted; the caoutchouc is simply immersed in a mixture of 40 parts of sulphide of carbon and 1 part of chloride of sulphur; it is next placed in a room heated to 21°, and when all the sulphide of carbon has been volatilised, the process is in so far complete that it is only requisite to boil the material in a solution of 500 grms. of caustic potassa to 10 litres of water, the vulcanised caoutchouc being next washed to remove excess of alkali. Recently (1870) Humphrey has introduced the use of petroleum ether (benzoline) instead of sulphide of carbon, as the former fluid dissolves chloride of sulphur readily. H. Gaultier de Claubry (1860) vulcanises caoutchouc by the aid of bleaching-powder and flowers of sulphur. This mixture produces chloride of sulphur, and the caoutchouc treated by it contains some chloride of calcium. Neither this process nor that of Gérard—the use of a solution of pentasulphide of potassium of 25° to 30° B., aided by a temperature of 150°, and a pressure of 5 atmospheres or 75 lbs. to the square inch—are practically available on the large scale. Articles of vulcanised india-rubber are made of ordinary caoutchouc and then vulcanised. The uses of vulcanised india-rubber are so many and so generally known that it is hardly necessary to enumerate them.

In the year 1852 Goodyear discovered a process by which caoutchouc is rendered hard and woodlike, being then termed vulcanite or ebonite. This substance exhibits a black or brown colour, and is largely used for making combs, imitation jet ornaments, stethescopes, and a variety of articles. The preparation of ebonite differs from that of vulcanite only in the introduction of a larger amount of sulphur (30 to 60 per cent), at a higher temperature, with the addition of other substances, shellac, gutta-percha, asphalte, chalk, sulphate of baryta, pipe-clay, sulphurets of zinc, antimony, or copper, &c. Ebonite is capable of taking a high polish; does not, as is the case with horn, become rough when cleaned with hot water, and is to some extent elastic. Vulcanised caoutchouc mixed with sand, emery, and quartz, is used for sharpening agricultural implements, scythes, sickles, &c.

Production and Consumption of Caoutchouc. The total quantity of caoutchouc produced in 1870 amounted to 120,000 cwts., of which the island of Java yielded 60,000 cwts. The consumption is fully equal to the supply, the largest quantity being used in North America, 35,000 cwts.

Gutta-Percha. Plastic gum, gutta or getah-percha, gettannia gum, tuban gum, is a substance in many respects similar to caoutchouc; it is the inspissated juice of the

Isonandra gutta, a tree growing in Malacca, Borneo, Singapore, Java, Madura, and adjacent countries.

Gutta-percha was at first obtained by felling the trees and collecting the exuding juice, either in suitable vessels or in shallow pits dug in the soil, or in baskets made from banyan leaves, the juice being left to coagulate under the action of the sun. More recently deep incisions are made in the trees and the exuding juice collected. The lumps of solid gutta-percha thus obtained are united by softening in hot water and by pressure. The raw gutta-percha of commerce is a dry, red, or marbled mass, not unlike leather cuttings which have been pressed together; the raw material contains as impurities some sand, small pieces of wood and bark, and sometimes other inspissated vegetable juices of less value than gutta-percha. The name gutta-percha really means Sumatra gum, this island being known in Malay language as Pulo-percha. When perfectly pure gutta-percha is quite white, its ordinary brown colour being due to an acid insoluble in water, which is present, partly free, partly as insoluble salts (of magnesia, ammonia, potash, and protoxide of manganese), of apocrenic acid; but in addition there is a small quantity of organic colouring matter. Gutta-percha is a mixture of several oxygen-containing resins, which appear to be the products of the oxidation of a hydrocarbon, the formula of which is $C_{20}H_{60}$. Payen found in gutta-percha the following substances:—75 to 80 per cent of pure gutta-percha; 14 to 16 per cent of a white crystalline resin termed alban; and from 4 to 6 per cent of an amorphous yellow resin named fluavil. Previously to being used gutta-percha is cleansed from dirt by a mechanical process of kneading in warm water, being then usually rolled into thick plates or sheets. The purified material exhibits a chocolate-brown colour, is not transparent unless first reduced to sheets as thin as paper, when the gutta-percha is in transparency equal to horn. At the ordinary temperature of the air gutta-percha is very tough, stiff, not very elastic nor ductile. Every square inch of a strap of gutta-percha, if of good quality and as homogeneous as possible, can sustain a strain of 1872 kilos. without breaking. Its sp. gr. = 0·979. At 50° it becomes soft, and at 70° to 80° it is so soft as to be very readily moulded, while two pieces pressed together at this temperature become perfectly joined. By the aid of heat gutta-percha can be rolled into sheets, drawn into wire, and kneaded into a homogeneous mass with caoutchouc.

Solvents of Gutta-Percha. Gutta-percha is insoluble in water, alcohol, dilute acids, and alkalies; it is soluble in warm oil of turpentine, sulphide of carbon, chloroform, coal-tar oil, caoutchouc oil, and in the somewhat similar oil obtained by the dry distillation of gutta-percha. Ether and some of the essential oils render gutta-percha pasty. As already stated this substance becomes soft in hot water, absorbing a small quantity, which is only very slowly driven off. Dry gutta-percha is a very good insulating material for electricity.

Uses of Gutta-Percha. The natural properties of this substance indicate its use as a substitute for leather, papier maché, cardboard, wood, millboard, paper, metal, &c., in all cases not exposed to the action of heat, and where a substance is desired resisting water, alcohol, dilute acids, and alkalies. The raw material, previously to being moulded into shape, is purified and kneaded by means of powerful machinery and with the assistance of hot water (some soda or bleaching-powder solution being added), the aim being the removal of such impurities as are only mechanically mixed with the gutta-percha as well as the removal of some of the colouring matter, while a more homogeneous mass is produced. The purified substance is next submitted to the action of kneading machinery similar to that in use for working up caoutchouc, while it is rolled out into plates of some 3 centimetres in thickness. Gutta-percha is moulded into tubes by the aid of machinery similar to that employed for making lead and block-tin tubing. Many objects are made from gutta-percha by pressing it while soft into wooden or metal moulds. By the use of a solution of gutta-percha in benzol, it may be glued to leather and similar substances. It is almost impossible to enumerate the various uses of gutta-percha. It is employed for straps for machinery instead of leather, tubes for conveying water, pumps, pails, surgical instruments, ornamental objects of various kinds, for covering telegraph wires, &c. Unlike pure caoutchouc gutta-percha becomes gradually deteriorated by exposure to the atmosphere, so that it can be even readily ground to powder.

Mixture of Gutta-Percha and Caoutchouc. Frequently a mixture of 1 part of gutta-percha and 2 parts of caoutchouc is employed. Articles made of this compound possess the properties of both substances, and may be vulcanised equally as well as gutta-percha alone. A mixture of equal parts of caoutchouc, gutta-percha, and sulphur, heated for several hours to 120°, obtains properties similar to those of bone and horn. Sometimes gypsum, resin, and lead compounds are added to this mixture, which is then used for making knife hafts, buttons, &c.

Varnishes. By varnish we understand a liquid of an oily or resinous nature employed for coating various objects, the thin film becoming dry and hard, thus protecting the object on which it is laid from the action of air and water, and at the same time imparting a glossy and shining surface. We distinguish oil and spirit varnishes. **Oil Varnishes.** Oil varnishes are usually prepared from linseed oil, but sometimes, especially for artist's purposes, poppy seed and walnut oil (so-called drying oils) are used. Linseed oil (raw) becomes slowly converted by the action of the air into a tough, elastic, semi-transparent mass; but this property is possessed in a far higher degree by the so-called boiled oil, that is to say—an oil which has been brought by the action of heat and of oxidising materials into a state of greater activity, in fact—into a state of incipient slow oxidation, the result of which is the formation of the substance termed by Dr. G. J. Mulder* linoxine, which in many of its properties corresponds to caoutchouc. The drying of oil varnishes is not therefore due to evaporation (leaving, as is the case with alcohol varnishes, a coherent film of resin), but to the oxidising action of the oxygen of the air, whereby a coherent film of linoxine is formed. Linseed oil (raw) is converted into what is termed varnish by heating the oil with certain substances which more or less readily give off oxygen, while these substances also act upon the elaine, palmitine, and myristine of the linseed oil. The greater part of the linseed and other drying oils is linoleine, $3(C_{32}H_{27}O_5),C_6H_5O_3$, which by slow oxidation becomes linoxine $= C_{32}H_{27}O_{11}$, by the action of alkalies converted into linoxic acid, $HO,C_{32}H_{25}O_9$. The substances with which raw linseed oil is boiled are litharge, oxide of zinc, and peroxide of manganese. It is certainly preferable to carry this operation into effect upon the water bath, or at least with vessels provided with steam jackets. The oxides are employed in coarse powders, which are suspended in a linen bag in the oil. In practice 1 part of oxide of zinc or litharge is taken to 16 parts of raw oil; and of the manganese 1 part to 10 of oil; the oxides become partially dissolved in the oil, while they aid in converting the palmitine, &c. (not linoleine), into plaster (lead or zinc soap). Boiled linseed oil usually contains from 2·5 to 3 per cent of litharge dissolved. Neither the addition of sulphate of zinc nor such absurdly added substances as onions, bread crust, or beet-root have any result whatever. Linseed oil intended to be mixed with zinc-white should not be boiled with litharge, but with peroxide of manganese. The lower the temperature at which linseed oil is boiled the brighter its colour. Mulder found that when raw linseed oil, especially if old, was kept for 12 to 18 hours at a temperature of 100°, it acquired the property of boiled oil. Sometimes after boiling linseed oil is bleached by exposing it in shallow trays

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* This author published some years ago in the Dutch language a highly interesting and valuable work—practically as well as scientifically—on the drying-oils.

10 centims. deep, best made of sheet lead, covered with sheets of glass, to the action of strong summer sunlight. Liebig's recipe for making a bright varnish is the following:—To 10 kilos. of raw linseed oil are added 300 grms. of finely pulverised litharge, after which there is added a solution of 600 grms. of acetate of lead; the mixture is vigorously stirred, and after the subsidence of the materials the clear varnish is ready for use. Borate of manganese is, according to Barruel and Jean, an excellent so-called siccative (dryer) when added to raw linseed oil, 1 part to 1000 of oil. Mulder's experiments confirm this statement in every respect.

Gold Size. This is used in gilding for fixing gold leaf on wood, paper, &c., and consists of a solution of linseed oil and lead plaster in oil of turpentine, prepared by first saponifying linseed oil with caustic soda or potassa, and precipitating the aqueous solution of the soap with a solution of acetate of lead, the lead soap thus formed being next dissolved in oil of turpentine.

Printing Ink. This is, when genuine and prepared from good linseed or walnut oil, anhydride of linoleic acid, $C_{32}H_{27}O_3$, mixed with very finely divided lamp-black, and obtained by heating raw linseed oil for several hours, at a high temperature (315° to 360°), whereby the fatty constituents—glycerine, palmitine, &c.—are volatilised. Usually the oil is heated in vessels directly exposed to the action of fire, and as the colour of the ink is black, a deep colour of the residue of the heating of the oil is not of much consequence. In order to render printing ink more rapidly drying, some borate of manganese may be heated with it at 315° for some hours. The quantity of fine lamp-black (best re-ignited in close vessels, or exhausted with boiling alcohol) usually added to printing ink, amounts to about 16 per cent. Soap is added in order to prevent smearing and assist in obtaining sharpness of impression. Coloured printing inks are obtained by adding to boiled oil red or blue or other pigments; for red vermillion is used. The ink used in lithography and copper-plate printing is made thicker, a better black being added.

Oil Varnishes. The so-called fat or oil varnishes are solutions of resins in boiled linseed oil mixed with oil of turpentine, benzol, or benzoline. Amber, copal, anime, gum dammar, and asphalte, are among the more ordinary resins employed for this purpose, the varnishes being made by melting, with the aid of gentle heat, the amber, copal, &c., to which, while liquid, boiling linseed oil is added. The cauldron in which this operation takes place should only be two-thirds filled; and the mixture of oil and resin kept boiling for ten minutes. The cauldron having been removed from the fire its contents are allowed to cool down to 140°, when the oil of turpentine is added. The quantities by weight are 10 parts copal or amber, 20 to 30 boiled linseed oil, 25 to 30 oil of turpentine. Black asphalte varnish is obtained in a similar manner by treating 3 parts of asphalte, 4 of boiled linseed oil, and 15 to 18 parts of oil of turpentine. Dark coloured amber varnish is not prepared from amber but from the residue (*amber colophonium*) of the distillation of the empyreumatic oil of amber and succinic acid left in the still from the preparation of succinic acid. These varnishes are the most durable, but they dry slowly and are more or less coloured.

Spirit Varnish. The so-called spirit varnishes are solutions of certain resins, viz. sandarac, mastic, gumlac (shellac), anime in alcohol, aceton, wood spirit, benzoline, or sulphide of carbon. Good spirit varnish ought to dry rapidly, give a glossy surface, adhere strongly, and be neither brittle nor viscous. As shellac is frequently employed, the name of lac varnish is sometimes given to these varnishes. The spirit, usually methylated spirit, ought to be strong, about 92 per cent. The solution of the resins is promoted by the addition of one-third of their weight of coarsely powdered glass for the purpose of preventing the resinous matter caking together, and being thus to some extent withdrawn from the solvent action of the alcohol. In order to render the coating remaining from the evaporation of the spirit less brittle, Venice turpentine is usually added. Sandarac varnish is obtained by dissolving 10 parts of sandarac and 1 of Venice turpentine in 30 of spirit. Shellac varnish, more durable than the former, is obtained by dissolving 1 part of shellac in 3 to 5 of spirits. French polish is a solution of shellac in a large quantity of spirits, and when this polish is to be applied to white wood, the varnish is bleached by filtration over animal charcoal. Copal varnish, far superior to the foregoing, is made by first melting the resin at as gentle a heat as possible so as to prevent the colouration of the substance, which is next pulverised, mixed with sand, treated with strong alcohol on a water bath, and filtered. A solution of turpentine or elemi resin is added to render the varnish softer. Colourless copal varnish is obtained by pouring over 6 kilos. of previously pulverised and molten copal, contained in a vessel which may be closed, 6 kilos. of alcohol at 98 per cent, 4 kilos. of oil of turpentine, and 1 kilo. of ether; the vessel containing this mixture having been closed is gently heated. The solution is clarified by decantation.

Coloured Spirit Varnishes. These are used chiefly for the purpose of coating instruments, and other objects of brass and coloured metallic alloys, so as to prevent the action of the atmosphere. Such varnishes are used for imparting a gold-colour to base metals; for this purpose alcoholic tinctures of gummi-gutta and dragon's blood, or fuchsin, picric acid, Martius yellow, and corallin, are separately prepared and added, in quantities found by trial, to a varnish consisting of 2 parts of seed lac, 4 of sandarac, 4 of elemi, and 40 of alcohol.

Turpentine Oil Varnishes. These are prepared in the same manner as the preceding. They dry more slowly, but are less brittle and more durable. Common turpentine oil varnish is obtained by dissolving ordinary resin in oil of turpentine; but this varnish is liable to crack. Copal is either dissolved in oil of turpentine, without or after having been melted; in the latter case the varnish being coloured. When non-melted copal is used it is broken into small lumps, and is suspended in a stout canvas bag over the surface of the oil of turpentine contained in a glass flask and placed on a sand bath, the vapours arising from the oil of turpentine gradually dissolving the copal. Dammar gum resin varnish made with oil of turpentine is prepared by drying the resin at a gentle heat and dissolving it in three to four times its weight of oil of tupentine. This varnish, though colourless, is not very durable. Green turpentine oil varnish is prepared by dissolving sandarac or mastic in concentrated caustic potash solution, diluting with water, and precipitating with acetate of copper, the dried precipitate being dissolved in oil of turpentine.

Polishing the Dried Varnish. In order to increase the gloss of varnished surfaces, especially on metallic objects and coaches, carriages and woodwork in theatres, concert-rooms, halls, &c., the dry surface is first rubbed over with soft felt, on which some very fine pumice-powder is laid, and is next polished with very soft woollen tissue on which some oil and rotten-stone is placed, the oil being rubbed off with starch-powder. Instead of varnishes, solutions of collodion (fulminating cotton in alcohol and ether) and solutions of water-glass are sometimes used; while Puscher recommends a solution of shellac in ammonia, largely used by hatters.

Pettenkofer's Process for Restoring Pictures. In order to remove the cracks often observed in old pictures, Von Pettenkofer has suggested exposure to the vapour of alcohol at the ordinary temperature of the air, the picture being placed in an air-tight box, at the bottom of which is a tray containing alcohol. This method has been tried, but not only has it failed in many cases, but some pictures have been actually spoiled. According to Dr. G. J. Mulder's researches, the only effective preservative of pictures is complete exclusion of air. He suggests that pictures should be well varnished on the painted side as well as on the back, and next hermetically covered with well-fitting sheets of polished glass on the front, and some substance on the back impermeable to air. The real cause of the ultimate destruction of pictures as well as of paint is the gradual but continuous, yet slow, oxidation of the linoxine, resulting in the crumbling to powder of the pulverulent matters—pigments, used as colours. It may not here be out of place to state that one of the best solvents of linoxine (dried paint) is a mixture of alcohol and chloroform, which may be advantageously used to remove stains of paint, and also of waggon and carriage grease from silk and woollen tissues.

CEMENTS, LUTES, AND PUTTY.

Cements. In a general sense we understand by cement, substances or mixtures which, when placed in a pasty state between the surfaces of bodies in close contact, cause them to adhere solidly after the drying or solidification of the pasty material. According to this definition, glue and paste are cements, but solder is not. As a universally applicable cement cannot be met with, it is clear that as regards any specific cement it should completely answer the purpose for which it is employed. The substances used for cement are very various, and are of course adapted to the particular objects they are intended to unite. There are numberless receipts for the preparation of cements, which may be best classified by stating the name of the most essential constituent. Thus we have:—1. Lime cements. 2. Oil cements. 3. Resin and sulphur cement. 4. Iron cements. 5. Starch, or paste. 6. Cements of less consequence, as, for instance, water-glass cement, chloride of zinc cement, &c.

Lime Cements. Slaked-lime forms with casein, white of eggs, gum-arabic, and glue, mixtures which after some time become very solid, and are used to unite wood, stone, metal, glass, porcelain, &c.

Casein cement may be made in various ways, but is most usually prepared by mixing freshly-precipitated casein, obtained by acidifying milk, previously freed from whey and separately reduced to powder, with freshly slaked lime. As this mass hardens very rapidly, it should be used immediately, and not prepared in larger quantity than may be required. Casein dissolved in bicarbonate of potash or soda solution, and gently evaporated to a thick consistency, also yields a good cement. A solution of casein in a concentrated aqueous solution of borax made with cold water yields a clear thick solution, which, as regards adhesive property, far surpasses a solution of gum-arabic. A solution of casein in silicate of soda or potash is an excellent cement for glass and porcelain. When stone, metal, wood, &c., are to be united, or when the cement is to be used for filling up small cavities, there is usually added to the mixture of casein and lime a powder made of 1 kilo. of fresh casein, 1 kilo. of quick-lime, and 3 kilos. of hydraulic mortar or lime. According to Hannon partly decayed and liquefied gluten yields with lime a cement similar to that obtained from casein.

Oil Cements. The main and essential constituent of these cements is a drying oil in the shape of an oil varnish (boiled linseed oil). Most of these cements resist the action of water.

Boiled linseed oil and fat copal varnish may be used as cements to unite glass and porcelain, but are seldom so employed on account of requiring some weeks to become dry. Mixed with white-lead, litharge, or minium (red lead), the cement dries more quickly, but does not become quite hard until after some weeks. When a larger quantity of this cement or rather putty, is required, it is frequently made of boiled linseed oil with a mixture of 10 per cent of litharge and 90 per cent of either washed chalk or slaked lime. Zinc-white is sometimes used instead of litharge. This putty is frequently warmed before use in order to render it softer; it is used for uniting stone, brick, &c. A mixture of 2 parts of litharge, 1 of slaked lime, and 1 of dry sand, made into a uniform paste with hot and boiled linseed oil, has been used by Stephenson as a putty to be placed into the sockets of steam-pipes. By precipitating a solution of soda-soap with alum solution an alumina soap insoluble in water is obtained, which, having been dissolved in warm linseed oil varnish, yields, according to Varrentrap, an excellent cement for uniting stone. Glaziers' putty is a mixture of chalk and boiled linseed oil, well beaten up together. When this putty is made with raw linseed oil it hardens very slowly; prepared with boiled linseed oil it may be kept soft for a considerable time by either being placed under water, or kept in bladders like lard, or tied up in canvas bags previously soaked with oil. According to Hirzel, a mixture of litharge and glycerine forms an excellent cement and readily hardening lute, which, according to Pollack, may even be used to unite iron and iron, as well as iron and stone.

Resin Cements. Cements made with resin as the main constituent are often used, because, on becoming cold, they harden at once and possess the property of being waterproof; on the other hand, these resin cements will not endure a high temperature without becoming soft, and by exposure to air and sunlight they become so brittle as to be easily pulverised.

As a cement for glass and porcelain, sandarac and mastic are sometimes used, because these resins are readily fusible and are colourless. They are applied to the surfaces to be united in the form of a powder put on with a small hair-brush, after which the object is heated so as to melt the resins, the pieces to be joined being pressed together. As far back as the year 1828, Lampadius suggested as an excellent cement a solution of 1 part of amber in 1·5 parts of sulphide of carbon. When this solution is painted over the surfaces to be united and immediately pressed together, the joint is at once effected owing to the rapid evaporation of the sulphide of carbon. A solution of mastic in sulphide of carbon may be similarly used. Shellac alone does not form a good cement, being too brittle when cold, and contracting too much after having been melted; the addition of some Venice turpentine and earthy powders (see Sealing-wax) compensates these defects. While wood cannot be joined together with shellac, it is firmly and readily glued by coating the pieces to be joined with thick shellac-varnish, and then placing between the two pieces a slip of muslin. Resins are frequently used for lining water-cisterns, and for rendering terraces, &c., waterproof. Pitch, colophonium, asphalte, mixed with lime, sulphur, or turpentine, are used for this purpose, the object of the various additions being to obtain a greater or less degree of hardness. Jeffery's marine glue is prepared by dissolving caoutchouc in twelve times its weight of coal-tar naphtha and adding twice the weight of either asphalte or shellac. The mixture is gently heated to render it uniform. There is a solid and a fluid marine glue in the trade; the former is used for glueing wood and for caulking, the latter, obtained simply by the use of a larger quantity of solvent, is used as a varnish; both kinds are insoluble in water, are not acted upon by change of temperature, and do not become brittle. By the name of zeiodelite is understood a mixture consisting of 19 parts of sulphur and 42 of powdered glass or earthenware; this mixture having been heated to the melting-point of sulphur, may be used, instead of hydraulic cement, for uniting stones and bricks. R. Böttger prepares this cement by mixing with molten sulphur an equal weight of infusoria earth to which some graphite is added. Under the name of diatite Merrick prepares a mixture of shellac and finely divided silica.

Iron Cement. Among the very many recipes given for the preparation of this cement, used for luting the sockets and spigots or flanges of cast-iron pipes, and for caulking the seams of the plates of steam-boilers, we quote the following as one of the best:—A mixture of 2 parts of sal-ammoniac, 1 of sulphur, and 60 of finely-pulverised cast-iron borings or filings. When required for use, this mixture is made into a paste with water, to which some vinegar or dilute sulphuric acid is added. The parts to be joined by this cement should be free from fat, oil, or rust. The cement is forced in with the caulking-chisel and soon becomes very hard. A lute for small leaks in iron and fire-clay gas-retorts can be made with 4 parts of iron-filings, 2 of clay, and 1 of pulverised porcelain saggers. This mixture is made into a paste with a solution of common salt.

Paste. The material used by bookbinders, and, in fact, wherever paper is to be glued to paper, is obtained by boiling flour with water or by treating starch with hot water.

Starch paste is best made by rubbing the dry starch up with cold water, so as to form a uniform magma, to which, while being constantly stirred, boiling water is very rapidly added; this paste should not be boiled if required for cementing paper together. Rye-meal boiled with water yields an excellent paste, which may be improved by the addition of some glue solution and preserved by alum. Partly decayed and liquefied gluten forms an excellent paste. Starch-paste to which, while hot, half its weight of turpentine is added is greatly improved and rendered waterproof by the addition.

DIVISION V.

ANIMAL SUBSTANCES AND THEIR INDUSTRIAL APPLICATION.

Woollen Industry.

Origin and Properties of Wool. Wool is distinguished from hair chiefly by the three following properties:—wool is finer; is not straight, but curled; while it generally contains less pigment, and hence is white in colour. The quality of wool increases with the increase of these three characteristics. Wool, like hair, exhibits an organised structure, consisting histologically of an epithelium, of a rind and of a pith or marrow. The epithelium of wool consists of small thin plates which overlap each other like the tiles on a roof; in this manner the cuticular plates give to the surface a squamose appearance, which may be coarsely represented as the appearance exhibited by a fir-cone. Fig. 251 exhibits a piece of wool of an ordinary sheep; while Fig. 252, magnified to the same number of diameters, exhibits a piece of the very finest Saxony wool, thus showing the great difference of fineness of these two sorts

Fig. 251.

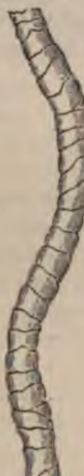
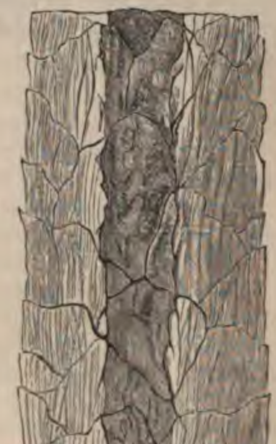


Fig. 252.



of wool. The grooves on the surface of the wool are the cause of its rawness to the touch, and from the existence of these grooves wool admits of being felted. When the fibre which exhibits this texture is pressed together with a kind of kneading motion, while the fibre is at the same time softened by the action of steam, the result is that the fibres are joined to each other in the direction of the scales on their surface and, becoming entangled, form a firm, dense texture, which is termed felt.

We obtain wool chiefly from sheep; the quality of the wool very much depends upon the peculiar breed, the climate, fodder, and care taken of the animals. We distinguish two chief breeds of sheep—viz.:—1. The mountain sheep, having short, fine, and more or less curly wool. 2. The sheep of the lowlands, having coarse, sleek, long, hair-like wool. To the first breed of sheep belongs the sheep met with in the interior and more elevated parts of Germany, also the Spanish merino sheep, of which there are several varieties, the most remarkable being the infantado and electoral races. By the latter is understood the variety which in 1765 was imported into Saxony, being made a present to the Elector, and was the cause of the existence in that country of a breed of sheep yielding excellent wool. Till comparatively recently the exportation of the living merino sheep from Spain was prohibited under pain of capital punishment. The variety of sheep designated Escurial is not a peculiar race or breed, but an electoral sheep with finer and fuller fleece. Sheep, like goats, are undoubtedly animals preferring a mountain plateau, and are very sensitive to a damp or moist soil. There are many varieties of the lowland sheep, among them the heath sheep (lowlands of Germany); the so-called Cretan goat (*Ovisaries strepsiceros*) of Southern Europe and Western Asia; the various breeds of English sheep, Southdown, Leicester, Cotswold, Lincoln, &c., and the Scottish varieties, Shetland and Hebrides.

The varieties of wool obtained from other animals than sheep are:—

a. Cashmere wool; the fine downy hair of the Cashmere goats inhabiting the eastern slopes of the Himalaya, 14,000 to 18,000 feet above sea level. The colour is white-grey or brown. In the state in which it is sent to Europe it is largely mixed with coarse hair, so that 100 kilos. of the raw material yield after sorting and cleansing only 20 kilos. of fine hair.

b. The Vicuna wool; the very slightly curly hair of the Llama or Vicuna goat (*Auchenia Vicuna*), a native of the high mountains of Peru, Chili, and Mexico. This kind of wool, or rather woolly hair, was formerly more so than now employed for weaving fine tissues. Sometimes there is substituted for this wool a mixture of ordinary wool and the finest hair of hares and rabbits. What is now termed Viguna or Vicuna wool in the trade is a tissue made of a mixture of wool and cotton.

c. Alpaca wool, or pacos hair; the long, sleek, white, black, or brown hair of the Alpagua or Alpaco (Pako), a kind of goat which dwells in Peru. This kind of woolly hair has great similarity with the Vicuna wool, but is not quite so fine.*

d. Mohair, or so-called camel's wool; the long, slightly curly, silky hair of the Angora goat (*Capra angorensis*), a native of Asia Minor. This substance is spun and woven into non-fulled tissues (camlet or plush), and is also mixed up with the half-silk tissues of which it forms the woof or weft.

Chemical Composition of Wool. Purified and cleansed wool consists chiefly of an albuminoid sulphur-containing substance termed keratin (horny matter), but, as met with on the animals, wool contains much dirt, dust, and suint. The labours of Faist, Reich, Ulbricht, Hartmann, Märcher, and E. Schulze have greatly increased our knowledge of this substance.

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* The microscopical texture and properties of this kind of hair have been investigated and are described in Wiesner's work, "Einleitung in die Technische Mikroskopie." Vienna, 1867, p. 172 *et seq.*

The following results are those obtained by Faist when analysing various kinds of merino wool:—

	1.		2.			
	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Mineral matter	6·3	16·8	0·94	1·3	1·0	1·2
Suint and fatty matter	44·3	44·7	21·00	40·0	27·0	16·6
Pure wool	38·0	28·5	72·00	56·0	64·8	77·7
Moisture	11·4	7·0	6·06	2·7	7·2	3·5
	100·0	100·0	100·00	100·0	100·0	100·0
Percentage of pure air-dry wool	49·4	35·5	78·06	58·7	72·0	82·2

1. Raw wool, air-dried.—*a.* Hohenheim wool, with a small quantity of readily soluble suint. *b.* Hohenheim wool (the name of a large agricultural establishment and agronomical school near Stüttgardt, Wurtemburg), containing a large quantity of glutinous suint. 2. Washed wool, air-dry.*—*c.* Hohenheim wool. *d.* Same variety, with difficultly soluble suint. *e.* Hungarian wool, very soft. *f.* Wurtemburg wool, less soft.

While making researches on wool, Elsner of Gronow estimated the loss which wool experiences when treated with sulphide of carbon for the elimination of the suint. The results were:—

Washed merino wool	15 to 70 per cent.
Unwashed wool (*laine en suint*, raw wool) ...	50 to 80 „
Long carded wool	18 „

Suint is a mixture of secreted and accidental substances, dust, &c. When raw wool is macerated for some time in warm water, there results a turbid liquid which contains suspended as well as dissolved matters. The dry substance of the aqueous extract of suint consists, according to Märcker and Schulze (1869), of:—

	1.	2.	3.	4.
Organic matter ...	58·92	61·86	59·12	60·47
Mineral matter ...	41·08	38·14	40·88	39·53

1 and 2 relates to wool of mountain sheep. 3 and 4 to full-bred Rambouillet sheep.

The soluble portion contains the potash salt of a fatty acid (*suintate de potasse*). The fatty acids contained in suint are, according to Reich and Ulbricht, mixtures of oleic and stearic acids, probably also palmitinic acid and a small quantity of valerianic acid, with potash in such quantity, that more recently this material has been employed to obtain therefrom carbonate of potash and chloride of potassium 100 kilos. of raw wool may yield from 7 to 9 kilos. of potash (See p. 132). Potash from suint consists, according to Märcker and Schulze, of:—

Carbonate of potash	86·78
Chloride of potassium	6·18
Sulphate of potash	2·83
Silica, alumina, lime, magnesia, oxide of iron, phosphoric acid, &c.	4·21
	100·00

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* Washed on the sheep while alive, an operation performed by the farmers, and to be distinguished from the washing wool undergoes during manufacture.

P. Havrez (1870) states that it is more advantageous to extract chloride of potassium and prepare ferrocyanide of potassium from suint than to employ it in preparing carbonate of potash. Suint is a valuable material in gas manufacture and the potash salts may afterwards be extracted from the coke.

Properties of Wool. The value and applicability of wool for the purposes of being spun and woven depend upon a number of properties, of which the following are the most important.

Colour and Gloss. Wool is generally white, but that of some of the common kinds of sheep and also of the alpaca and mohair are either brown, grey, or black. The gloss of some varieties of wool is a highly prized property. The gloss is not exactly related to the fineness of the wool, but more to the softness and suppleness of the fibre, which on being touched by the hand imparts a feeling similar to that of cotton-wool or silk. The curl or waviness of the wool is due to the fact that the hair or fibre is bent and more or less curved. When there are many and small curves the wool is termed small curled, while if the curves are large it is termed coarsely curled. There is also a difference between wool which exhibits high curves (strongly waved and curled) and wool exhibiting low curves (weakly waved and curled). The fineness of wool depends upon the smallness of diameter of the fibre; generally the finer the fibre the better the wool is suited for the uses commonly made of it. There are, however, some varieties of wool met with which, though very fine, are rather tough and straight, and therefore less suited for manufacturing purposes. It should be observed that the diameter of the woollen fibre does not constantly vary with the fineness; while neither the wool-meter (eriometer) nor the micrometer can sufficiently determine the fineness of the wool for technical purposes, that property being best estimated by practical experience by the sense of touch. What is termed quality or uniformity in wool is that the fibre has through its entire length the same diameter. By softness, suppleness of the wool, it is understood that the fibre readily admits of being bent in all directions; this property is usually accompanied by extensibility and elasticity. A fibre of wool may therefore be somewhat more strongly stretched before breaking, after it has been first straightened so as to remove the curls. The elasticity of the fibre is shown, when a hair is broken, by the two ends becoming more or less rapidly contracted and curled up. By strength we mean that property of wool whereby it bears without breaking a certain weight, which, according to the quality and fineness of the fibre, varies from 2·6 to 44 grms. By height is understood the length of the curled hair in its natural position; while by length we designate the measure (in centimetres) of a single fibre when so stretched that its curls are no longer perceptible. The length of the fibre is of great importance in the selection of wool, and constitutes one of the main distinctions between carded wool and short wool. The teasled wool is used more especially for the weaving of cloth—milled or fulled cloth. Generally this kind of wool is strongly curled, and the length of the stretched hair is less than * 15 centims. The combed wool (long wool) is used for smooth woollen tissues which require a middling length, 9 to 12 centims., some strength, and not too much curl.

Preparation of Wool. Before wool is a marketable article it has to be washed, shaved or sheared off, and sorted.

I. Just before shearing the wool is washed—or as the term more usually runs, the sheep are washed—for the purpose of cleansing the fleece and of eliminating a portion of the suint. By this washing wool loses from 20 to 70 per cent in weight.

metre = 3 4 7

1 centim = $\frac{39}{100}$

*6 —

[illegible]

II. *The Shearing of the Sheep.*—Usually in our climate sheep are shorn only once a-year, about the middle of May or beginning of June, but with long-woolled sheep this operation is performed in September (summer wool), and about the end of March (winter wool). Lamb's wool is distinguished by its great fineness. Besides the wool shorn from the live sheep we distinguish skinner's wool, from the skins of sheep slaughtered for food, and pelt wool from sheep which have died from disease; while the former kind is shorter than ordinary wool, the latter is deficient in strength and elasticity, and is therefore of less value.

III. *Sorting the Wool.*—The different parts of the skin of the sheep yield wool of different quality; among the parts which yield better kinds of wool are the shoulders, the flanks, and the thighs. The wool of the following parts is of inferior quality, viz., neck, withers, back, throat, breast, feet. The peculiar mode of sorting wool and the denominations given to the several varieties differ in different countries; generally the terms *firsts*, *seconds*, *thirds*, &c., are employed. While the fineness of the wool is the main character which distinguishes the various kinds, the sorter also looks to the length, curl, strength, &c. As met with in commerce, wool contains a larger or smaller quantity of hygroscopic water, varying from 14 to 16 per cent; and even when wool is exposed to dry air for a long time, the water amounts to 7 or 10 per cent.

Wool Spinning. The operations of spinning do not in strictness pertain to chemical technology, because the material operated upon is not chemically treated, and only mechanically undergoes a change of form. The machinery employed is very complicated, but has been brought to great perfection.

Before being made into cloth, the wool, as is the case with cotton, silk, flax, and hemp, has to be made into yarn. Before this operation can be proceeded with, the sorted wool is:—1. Carded for the purpose of weaving. 2. Or the wool is combed for the making of smooth woollen goods. Carded wool is ultimately made up into cloth, while combed wool is made up into such materials as thibet, mousseline de laine, merino, &c. The following eight operations are those to which carded wool is submitted:—

1. *Washing.*—The aim of this operation is to eliminate the suint from the wool, and for this purpose the fibre is submitted to the action of very weakly alkaline liquids. These even in the carbonated state should be weak, because, when concentrated, the wool either is dissolved or its strength and elasticity impaired. The alkaline liquids chiefly used for this purpose are lant (stale urine) mixed with water, tepid soap-suds, or a very weak solution of soda. The washed wool is rinsed in plenty of cold water, wrung out, and then dried in the shade. By exposure to direct sunlight wool becomes yellow. 100 parts of fleece lose by washing from 17 to 40 parts, leaving 60 to 83 parts of pure wool.

2. *Dyeing.*—When this operation takes place immediately after washing, it is only to impart to it very fixed dyes, such as indigo, or madder; because, as regards most other dyes, they would be injured by the operation of milling, in which soap, lant, and other materials are employed. Wool by being dyed often increases considerably in weight, sometimes as much as 12 per cent.

3. *Willowing, or Devilling.*—This operation aims at the obtaining of the flocks of wool in a more uniform mass, while at the same time mechanical impurities, straw, &c., are removed. The machinery by which this is effected is similar to that used for the same purpose for cotton.

4. *Oiling or Greasing.*—As wool has a great tendency to become felted, and has to be submitted to the operation of carding, it might in this process become broken; and in order to prevent this and give the fibre, which has become harsh, suppleness, it is greased or mixed with oil. For the finer kinds of wool, olive oil or arachis oil is used, while for coarser kinds rape-seed and fish oil are employed. Olein, as it is termed, really oleic acid, a by-product of the manufacture of stearine candles, is often used for this purpose, provided it be not contaminated with either sulphuric or stearic acids. 100 kilos. of wool for warp require 10 to 12 kilos. of oil, while 100 kilos. of wool for woof require 12 to 15 kilos. of oil.

5. The carding of wool aims at the same result as the carding of cotton. The machinery employed is in each instance similar in construction. Wool is carded at least twice. The first carding is termed fleece-carding, the result being that the wool is formed

into a loose fleece, which is rolled up on a cylinder; the second carding converts the fleece into loose curls about 1 metre or a yard in length, which are turned over on to the roving machine. Recently the carding-mill has been so constructed that it also performs the operation known as roving.

6. *Roving.*—By means of machinery the wool is converted into what is technically termed *slub* or *half-yarn*, which by the following operation, viz.,

7. By spinning is made into yarn. The machinery, while working at a high speed, twists the fibres into a continuous thread or yarn.

8. The finished yarn is wound on reels, the length of the skeins or hanks and the number of skeins to a bunch varying in different localities. The fineness of the yarn is abroad designated by the number of hanks which go to the half kilo.; but in Belgium and France the number of metres of yarn length which go to the kilo. expresses the fineness.

Artificial Wool. Woollen rags are carefully sorted, and by means of machinery converted into what is termed mungo and shoddy; the former is a short-haired wool obtained from milled goods; the latter (a longer hair) is prepared from woollen hosiery. The rags having been well sorted, and all seams, buttons, and ornaments cut off, silk and other linings separated, are cleansed, again sorted, and then oiled. The rags yield on an average 30 per cent of the weight of buttons, linings, &c., and the 70 per cent remaining yields some five-sevenths of mungo, prepared by means of a mill. Mungo is not carded; but shoddy, made by a similar process, is carded after having been again oiled.

Weaving the Cloth. Cloth is a smooth woollen fabric, the woof-yarn passing alternately over and under chain-yarns. The peculiar felty appearance is given to cloth by the operation of milling or fulling. The operation of weaving cloth does not differ in any way from the weaving of linen or cotton fabrics; usually the chain and weft yarn are equally fine.

Washing and Milling the Rough Cloth. The cloth as it leaves the weaver's hands is not in the least similar to the finished fabric, but is very like a coarsely woven towel, the chain and weft being quite loose and every thread distinctly visible; while the felty appearance of the cloth is entirely absent, this being obtained by the operation of milling, which is preceded by the burling process, whereby knots, pieces of straw, and other similar impurities are removed by the aid of small steel forceps. The rough cloth is next washed for the purpose of removing oil, dirt, and weavers' glue; this washing is assisted by soft soap, potash or soda ley, and is performed by a washing machine. The operation of fulling or milling aims not only at a cleansing of the rough cloth (it is not always washed previously to being milled), but more particularly at the felting together of the fabric, so that the chain and weft can hardly be distinguished. It is performed by the joint action of moisture, high temperature, and a peculiar mechanical treatment, by which the threads are kneaded into each other. As the milling also aims at the complete removal of grease the water into which the fabric is steeped is rendered alkaline by means of lant, while soft-soap and fuller's earth (see p. 295) are used to assist the action. Soft soap is only used for common cloth, while for the finer kinds palm oil and olive oil soaps are employed. The milling or fulling consists in beating the rough cloth with wooden mallets moved by machinery; recently the use of cylinders is very general for this purpose.

Teasling and Shearing the Cloth. In order to give to the milled cloth a more pleasing appearance, it is first teasled and next shorn. 1. The operation of teasling aims at the loosening of the surface hairs of the felted cloth, and at brushing these in one direction; the operation is performed by the use of teasles or weaver's thistle (*Dipsacus fullonum*) which acts by the thorns on the seed capsules. 2. The shearing of the cloth is an operation by which the surface hair is cut off to a uniform length. The shearing is either performed by hand—a very tedious operation, the cloth being stretched uniformly on a cushioned table, the operator using peculiarly made shears—or by cylinders, somewhat similar to lawn grass-cutters in principle of working. There is a distinction between transversal, longitudinal, and diagonal cylinders. *α.* The transversal cylinder is placed lengthwise to the cloth, the cylinder moving from one edge of the cloth to the other. *β.* In the longitudinal machine the moving cylinder is placed across the width of the cloth, which is moved under the shearing-knives. γ. In the diagonal machine several cutting cylinders are placed diagonally above the cloth. The wool shorn off is used in upholstering, and very largely for the purpose of giving a velvety appearance to some kinds of paper-hangings.

Dressing the Cloth. Before the cloth is ready for sale, it has to be submitted to the three following operations:—Lustring, brushing, and pressing.

1. The lustring is now performed by stretching the cloth very tightly on a copper cylinder, the surface of which is perforated with a number of small holes. The cylinder is placed in a steam chest, and steam having been turned on, the cloth obtains a permanent gloss and is prevented from becoming rough on being worn. 2. The brushing of the cloth takes place before and after the shearing, and is effected by machinery, the

brushes being fixed to cylinders, and the cloth moved over and under them, while at the same time either a jet of water or sometimes steam is made to play on the cloth. 3. Finally, the cloth is pressed, having been first folded; between each fold is placed on the right side of the cloth a piece of glazed millboard and a piece of coarser millboard on the wrong side; a plank is put between the pieces of cloths, some six to twelve of which are placed in the press at a time.

Other Cloth Fabrics. In addition to milled cloth several other kinds of woollen goods are manufactured, which are cloth-like in some particular. Of these the following are the chief:—Flannel, either smooth or twilled, only slightly milled, once teasled on the right side, and either not shorn at all or only once; the chain often consists of carded wool, but is sometimes cotton or silk; the woof is carded yarn. Swan-skin is fine twilled flannel. Cashmere is finely twilled cloth only once teasled, but shorn as often as cloth. The hair is short and covers the textile yarn slightly, so that the twill is distinctly seen. Cashmere is often made with a cotton chain.

Frieze is coarser, stouter, and longer-haired than cloth, is strongly fulled, but less teasled and also less shorn. After having been shorn, frieze is simply dressed by being brushed and hot-pressed; it is then brushed over with a solution of tragacanth in water, next calendered, and lastly slightly oiled with olive oil and again pressed. A non-twilled and finer kind of frieze is known as "ladies' mantle frieze;" while a heavier and short shorn frieze is called castories. Kalmuk and thick frieze (Irish frieze) consists of a heavier yarn and is more strongly milled. Buckskin is a twilled non-teasled trouser material, the right side of which is shorn and quite smooth. Kersey is a coarse kind of undressed (neither teasled nor shorn) woollen fabric used for making cloaks and overcoats for military men, sailors, railway officials, &c. The coarser kinds of railway rugs and horse-cloths are of a similar material. Paper-makers' felt is a coarse, twilled, loosely woven, lightly milled material, neither teasled nor shorn, used for the purpose of being placed between the wet sheets of paper. Felted cloth, a fabric first made some twenty years ago without spinning and weaving at all, has not been found suitable, and is therefore now hardly ever seen. Wool intended for felting purposes is first cleansed, freed from suint, next carded and converted into a uniformly thick layer similar to cotton-wool, and is then felted.

Worsted Wool. It has been already stated that long haired or combed wool is the material used for the purpose of preparing worsted-yarn—a smooth thread, the longitudinal fibres of which are placed parallel to each other—this yarn serving the purpose of weaving such fabrics as thibet, merino, Orleans, &c. There is a distinction between genuine combed wool or worsted, and half-worsted or sayette-yarn, which is the link, as it were, between combed and carded wool, and is used for the purposes of knitting stockings, in carpet-making, Berlin-wool work, &c. Although half-worsted is always spun from long-haired wool, the fibre is not in this instance combed, but carded by a peculiarly constructed mill. Combed yarn or worsted consists either entirely of wool, or is a thread of wool mixed with mohair and alpaca, or of wool and cotton, or of wool and silk, such yarns being termed fancy yarns.

The manufacture of smooth woollen fabrics is, as far as weaving and the mechanical operations are concerned, similar to the weaving and mode of manufacturing other textile fabrics. Some of the smooth-surfaced woollen fabrics are finished when woven; others require a dressing which depends upon the taste of the consumers and upon the peculiar requirements of the trade. The following enumeration of the smooth-surfaced woollen fabrics, of which there is an almost endless variety, may give some idea of the various kinds of goods belonging to this category.

A. *Smooth Fabrics.*—Barracan used to be formerly woven from camel's hair, but is now woven from combed wool; it is termed moiréd when it is watered. Orleans consists of a twisted cotton thread chain and a single woollen weft; the fabric having been woven is singed, washed, dried, shorn, and hot-pressed. Camlet also was formerly made from camel's hair, and consists of combed woollen chain and weft. Dress crape is a fabric made of a strongly twisted worsted yarn-chain and more loosely woven weft; when the cloth is woven it is dyed black or grey, next wound round a cylinder, and boiled in water in order to shrink it. Bolting cloth is made of a strongly twisted yarn, and employed for the purpose of making flour-sieves. Mousseline de laine, chaly, is a woollen muslin with silk chain, and this class includes a host of fabrics generally known as Bradford fabrics as well as mixed materials, alpaca, mohair, silk mohair, &c.

B. *Twilled Goods.*—Merinos with three- or four-threaded twill and two "right" sides are, after weaving, singed, hot-pressed, and dressed or glazed. When unglazed it is called thibet. Serges are twilled fabrics with three, four, or five strands. So-called Atlas fabrics are kalmang and lasting, the latter employed for ladies' shoes, gentlemen's cravats, furniture, and upholstery work. The fabric from which the press-bags of the oil-mills are made is also a twilled woollen material woven from very strong and tough wool.

C. *Variegated or Patterned Fabrics*, such as are used for trousers, and also woollen damask. Shawls belong to this class; in some of these the whole fabric is woollen (Cashmere shawls); in others a silk or cotton thread is mixed. The plaids and tartans are especially British fabrics.

D. *Velvets.*—Woollen velvet, woollen plush, and velpel, are merely distinguished from each other by the length of the hair, which is greater in plush than in velvet, and greatest in velveteen. Woollen velvets are employed in various ways; for instance, in covering chairs, sofas, for curtains, &c. These materials are more or less loosely woven, and are variously shorn and dressed, being known in the trade by such appellations as astracan, beaver, castorin, Utrecht velvet, &c.

Silk.

Silk. Silk is at once distinguished from cotton, flax, hemp, and wool by being naturally produced as a very long and continuous thread, whereby the operation of spinning is dispensed with; but in its stead the operation known as silk-throwing is required, by which several of the natural fibres of the silk are twisted into one in order to obtain a stouter yarn.

Silk is the produce of the silkworm (*Bombyx mori*), an insect which undergoes four metamorphoses. The worm is produced, in the spring, from the egg, or ovule. It casts its skin from three to four times, and finally spins a thread, produced, or rather secreted, by two glands placed near the head, from small apertures, in which is a glutinous fluid which immediately coagulates under contact with air. Thus what is termed a cocoon is formed, which serves as a shelter for the pupa against injury and cold. The thread is double, but is united in one by a peculiar kind of glue termed serecin, which is laid as a kind of varnish over the whole surface of the thread, of which it forms about 35 per cent of the weight. After a period of fifteen to twenty-one days the pupa is metamorphosed into a butterfly, which, in order to leave its prison, softens a portion of the cocoon with a juice which it secretes, and then perforates the softened part. For the purpose, however, of producing silk, the pupa is not allowed to develop so far, but is killed (excepting in a number of cocoons intended for the full development of the butterflies so that they may produce eggs), and the thread of the cocoon is carefully wound on a reel.

Sericiculture. Varieties of Silkworms. The *Bombyx mori* is the main supplier of silk. Its food is the leaves of the white mulberry tree, *Morus alba*. There are, however, other silk-producing insects, among which the following are to be noticed:—

a. Bombyx cynthia, largely cultivated by the natives of the north-east portion of the interior of Bengal and also by the Japanese; the former call this worm *Arrindy-arria*, the latter *Yama-maï*. This worm feeds on rice leaves, *Ricinus communis*. The silk obtained from this insect, although less brilliant than that which the ordinary silkworm yields, is very useful, as being durable and strong. This worm will feed on other leaves, such as that of the weavers' thistle, *Dipsacus fullonum*, wild chicory, *Chicorium Intibus*, and the leaves of the *Aylanthus glandulosa*. The results of acclimatising this insect in France and Germany have been satisfactory.

b. Bombyx Pernyi is a native of Mongolia and China; it feeds on oak-leaves. Some years ago these worms were introduced into France, and have been fed and reared successfully upon European oak-leaves.

c. Bombyx mylitta, or Tussa worm, is a native of the colder parts of Hindostan and of the slopes of the Himalaya. Its silk is an important article of commerce in Bengal. This insect feeds on oak and other leaves, casts its skin five times, and yields large cocoons. The fibre of this kind of silk is from six to seven times stouter than the silk of the ordinary worm, but unfortunately the Tussa worm only lives in its free natural state, and when captive does not produce silk. The following silk-producing varieties belong to North America:—*d. Bombyx polyphemus*; on oak and poplar trees. *e. B. cecropia*; on elm, whitethorn, and wild mulberry trees. *f. B. platensis*; on a kind of mimosa, *Mimosa platensis*. *g. B. leuca* deserves further attention.

We quote the following account of the culture and rearing of silkworms:—1. The mulberry tree. The leaves of the variety known as the white mulberry tree, from the fact that its fruit is yellow or light red in colour, is the most suitable food for this insect, but its cultivation belongs to horticultural pursuits, and we cannot enter upon the subject here. 2. The production of the eggs or ova of the silkworm is effected in the following manner:—The largest and finest cocoons, and such as have a fine thread, are selected and preserved; usually the cocoon of the female insect is more oval than that of the male, which is more pointed at the ends and is somewhat depressed in the centre. Although these characteristics do not apply in all cases, sericiculturists become sufficiently adepts in this matter to be able to select a sufficient number of cocoons of each sex. 100 to 120 pairs of well-formed cocoons yield about 30 grms. of eggs, about 50,000 in number, from which, however, only about 70 to 75 per cent of worms are obtained. The cocoons selected for breeding purposes are allowed to remain on a table covered with a white cotton cloth. After some twelve days the butterflies make their appearance, and having paired, the females after a lapse of some forty hours lay 300 to 400 eggs. 3. The eggs are properly protected from cold in winter and remain in the buildings, called *magnaneries*, being placed in a uniform layer on a cotton cloth stretched on a wooden frame. The eggs are covered with sheets of white paper perforated with small holes. Upon the sheets of paper mulberry leaves, at first cut up so as to form a kind of chaff, are placed. In France a contrivance known as a *couveuse*, that is to say, an oven in which a suitable temperature is kept up, is now generally used for the purpose of breeding the worms, which are best hatched from the eggs at a temperature of 30°, provided moisture is also present. The young brood on leaving the eggs creep through the holes in the paper, and seeking daylight (there is always free access of light in magnaneries) begin at once to feed on the mulberry leaves. 4. The rearing of the worms requires care and attention. They are best placed on paper laid on wooden frames. The worms grow rapidly and are very voracious. They cast their skins four times, and after thirty to thirty-two days begin to spin the cocoons. 5. When the period of spinning approaches, the worms are placed in small, somewhat conical wicker-work baskets, in which they are comfortably located. The first thread spun, or rather an entangled flocky mass, is afterwards separately collected and kept as floss silk. The insect discharges, before beginning to spin further, first a solid substance, white or green in colour, and consisting, according to Péligot, chiefly of uric acid, next a clear, watery, very alkaline liquid, which contains 1·5 per cent of carbonate of potash, this curious discharge amounting to 15 to 20 per cent of the weight of the worm. The formation of the cocoon is finished in about five days, but the cocoons are not collected for the purpose of reeling the silk until after seven or eight days, so as to make sure that all the worms have spun.

As far as the chemical composition of silk is concerned, we have to distinguish between the fibre and its envelope. The fibre consists for about half its weight of fibroin, a substance which, according to Städeler's researches, is nearly related to horny matter and mucus, and is identical with these as regards chemical composition. The formula of silk fibroin is $C_{15}H_{23}N_5O_6$. The gum-like envelope of the silk fibre, which has been termed by Cramer and Städeler silk glue or sericin, is partly soluble in water and readily so in soap-suds and other alkaline fluids. The formula of sericin is $C_{15}H_{25}N_5O_8$. P. Bolley's researches have proved that in the silk-producing and secreting glands of the worm only glutinous, semi-liquid fibroin occurs, which, in coming into contact with air, is acted upon by the oxygen and then converted into sericin. Raw silk leaves on ignition a small quantity of ash; Guinon found in Piedmontese raw silk, dried at 100°, 0·64 per cent of ash, consisting of 0·526 lime and 0·118 alumina and oxide of iron. Dr. G. J. Mulder found in 100 parts ofraw silk:—

	Yellow silk from Naples.	White silk from the Levant (Almasin silk).
Fibroin	53·40	54·0
Glue-yielding matter	20·70	19·1
Wax, resin, and fatty matter...	1·50	1·4
Colouring matter	0·05	—
Albumin	24·40	25·5

6. *Killing of the Pupa in the Cocoon.*—The pupa remains in the cocoon for from fifteen to twenty days, and is then metamorphosed into a butterfly, which will perforate the cocoon and thus obtain an exit. It is clear, however, that the cocoons not intended for breeding purposes should not be kept so long, because by the perforation of the cocoon the silk is spoiled, or at least greatly deteriorated; therefore the pupæ in the cocoons are killed either by the application of oven-heat or of steam.

Manipulation of the Silk.

Six different operations are required to render raw silk fit for use as an article of commerce and suited for weaving, &c. These operations are:—

1. The sorting of the cocoons, an operation which requires great care and greater experience, its aim being—(α) the separation of yellow from white cocoons; (β) the elimination of all damaged cocoons as only fit for yielding floret silk; the damage may arise in various ways, as, for instance, by mouldiness, injury by other insects, and, lastly, fouling of the pupa, as well as perforation by the butterfly; (γ) selection of the cocoons according to varying fineness of thread and uniformity of the silk.

2. Winding the silk on a reel is the first operation with the cocoon. By this the threads of silk which the insect has wound up into a kind of ball is wound off and brought into the shape of a skein or strand.

As the single fibre of silk is far too thin to be manipulated, the operator usually unites from 3 to 10 or even 20, making them unite by the operation of reeling; this is not by any means so readily performed as might be imagined, because it is difficult to find the end of the thread, whilst the surface of the cocoon is varnished with a gum-like mass which glues the fibres together. Partly by the aid of hot water and partly by dexterity these difficulties are overcome, and by good management a thread of 250 to 900 metres length may be obtained from each cocoon, each yielding from 0·16 to 0·20, at the utmost 0·25 grms., of raw silk. 1 kilo. of raw silk requires from 10 to 12 kilos. of cocoons. The silk thus obtained is termed raw silk, which should be quite uniform as regards thickness and strength of fibre. That portion—the interior and a portion of the outer layer of the cocoon—which does not admit of being reeled off is employed for making floret silk, by operations similar to those in use for wool and cotton—viz., cleansing, disentangling, combing, carding, and spinning, to produce a silk yarn.

1. *The Throwing of Silk.*—As the thread obtained by reeling is too fine for use either for weaving, knitting, sewing, &c., it is usual to unite several threads of silk by means very similar to those used in rope-making, an operation termed throwing, known as twisting when the thread of raw silk is simply rotated on its axis so as to make it stronger. The following are the chief varieties of thrown silk:—1. Organzine, used as chain for woven silk fabrics, is prepared from the best raw silk. The threads of 3 to 8 cocoons are united; being first strongly twisted and next thrown, after which two of such threads are twisted together. 2. Trame used for woof or weft and for silk cord is made from inferior cocoons. Single-threaded trame consists of one single twisted raw silk thread made up of the united threads of 3 to 12 cocoons. The double-threaded trame consists of two untwisted threads thrown to the left but less strongly than in organzine. There is also three-threaded trame, &c. Trame is softer and smoother than organzine, and therefore fills better than round threads in weaving. 3. Marabou silk is stiffly thrown and similar to whipcord; it is made from three threads of the whitest raw silk and thrown in the trame fashion; is dyed without being previously scoured (boiling the gum out in this instance), and is again thrown after dyeing. 4. Poil silk is a simple raw silk thread, twisted, and used chiefly as a basis for gold and silver wire, such as is worn on military uniforms. 5. Sewing silk is obtained from some 3 to 22 cocoon threads being twisted together. There are several other varieties of silk thread used for crochet, knitting, &c.

4. *Conditioning or Testing of Silk.*—The fineness of raw as well as of thrown silk is expressed by stating how many yards' or metres' length of the fibre are contained in a certain weight. The unit abroad is 400 ells or 475 metres. When the expression is used, that such silk is at 10 grains, it is understood that 475 metres' length of that particular silk weigh 10 grains; a silk at 20 grains has the same length but double the weight, and consequently that silk is only half as fine as the former.

Raw, as well as thrown silk, contains a large quantity of hygroscopic water, the quantity of which cannot be judged by the external appearance of the material. The silk usually met with in commerce contains 10 to 18 per cent of hygroscopic water; and silk may occasionally contain even 30 per cent without appearing to be moist. As silk is a very expensive material and often sold by weight, it is clear that this property of taking up water is too important to be left unnoticed; and for that reason silk is conditioned as it is called, that is, the quantity of water it contains is duly ascertained.

5. *Scouring or Boiling the Gum out of Silk.*—Excepting a few instances, such as for example, in the weaving of fine silken sieve cloths, and for crape and gauze

fabrics, raw silk has to be deprived of its envelope—the gummy matter already mentioned, in order to give softness, suppleness, gloss, and especially also to render the silk fit for being dyed.

The operation of scouring is comprised in the following manipulations:—

1. Removing the gum (*dégommer*).
2. Boiling.
3. Colouring.

The taking out of the gum is performed in the following manner:—Olive oil soap is first dissolved in hot water and into this solution at 85° the skeins of silk are placed hung on sticks. The skeins are moved about in this bath until all the gum has been uniformly taken out. The silk is next wrung out, rinsed in fresh water and then dried. Silk may by this process lose 12 to 25 per cent in weight, according to the quality of the raw silk and the quantity of soap employed. The scoured silk is ready for dyeing with dark colours, but if required to be dyed with bright colours it has to be first boiled. To this end it is put into coarse canvas bags, each containing from 12 to 16 kilos. of silk, and in these sacks the silk is placed in a soap bath and boiled for 1½ hours; the silk is next rinsed in water, wrung out, and dried. The operation of rosing or colouring aims at imparting to the silk a slight tint in order to enhance its beauty. The trade distinguishes various hues of white silk, such as Chinese white, azure white, pearl white, &c. The first of these hues, a somewhat ruddy tint, is obtained by rinsing the silk in soap-water, to which some Orleans has been added. The bluish hues are produced by indigo solutions. The bleaching of scoured silk is effected by the aid of sulphurous acid, the fibre either being placed in a room where this gas is evolved from burning sulphur, or by treating the silk with an aqueous solution of the acid. As silk loses a great deal in weight as well as in body by the scouring, which is, however, required, because raw silk does not admit of being dyed, it has become the practice to produce a material called *souple*, obtained by treating the raw silk with boiling water in which only a small quantity of soap, 1 kilo. to 25 kilos. of silk, is dissolved. Instead of this soap solution, an acidified (with dilute sulphuric acid) solution of sulphate of magnesia or of soda is sometimes used. The silk loses by this process only 4 to 10 per cent in weight. In order to bleach raw silk without depriving it of its natural rigidity, the skeins are digested at a temperature of 20° to 30° with a mixture of alcohol and hydrochloric acid; this liquor becomes green in colour, and the deeper the hue the whiter the silk. The silk is rinsed in water, and having been dried will be found to have lost only about 2·91 per cent in weight. The alcohol used in this process may be readily recovered by neutralising the acid with chalk and by subsequent distillation.

Weaving of Silk. This branch of the silk industry is very similar to the weaving of cotton, linen, woollen, and mixed fabrics; very frequently, however, silk yarn is mixed and woven with other fibres. Often either the chain or woof is made simply of twisted, not of thrown, silk, the advantage being the production of thicker, but less coarse fabrics. Dark silk tissues are ready for the market as soon as woven; they are only folded and pressed. Lighter silk fabrics (atlas and taffetas) are washed over with a sponge dipped in a solution of gum tragacanth, and are next hot-pressed or calendered by the aid of iron cylinders either heated by steam or by placing a red-hot iron in them. Heavy silk fabrics are often, as it is termed, *moiréd*, that is, while partly moistened are passed between hot rollers. By the aid of copper cylinders bearing various designs, different patterns are *en relief* embossed upon heavy silken and silk velvet fabrics, being *gaufred*, as it is termed.

Silk fabrics are:—1. Smooth. 2. Twilled. 3. Patterned. 4. Gauze. 5. Velvet.

a. To the first category belong:—1. Taffetas, a light, thin, smooth tissue, made of scoured silk, the chain being organzine single threaded, the woof trame, and bi- or tri-threaded. 2. Gros (*Gros de Tours, Gros de Naples*), a heavy taffetas-like fabric, woven with heavy thread, and hence having a ribbed appearance when thick and thin threads are mixed.

b. Twilled fabrics are:—1. The various kinds of serges (*Croisé, levantin, drap de soie, bombasin*). This fabric has a right and a wrong side, the former being the chain side. 2. Atlas, or satin, in all its endless varieties, single, double, half, and serge atlas.

c. Patterned fabrics. To this class belong all fabrics which either by the art of weaving or by other means are distinguished by some design (droguet, chagrin, reps, silk damask, &c.)

d. To the velvet fabrics belong:—1. Genuine velvet; cut or uncut. 2. Plush.

e. To the silk gauzes belong an immense variety of very light materials, as for instance:—1. Marle. 2. Silkstramin. 3. Crape. 4. Various qualities of silk webs. 5. Barège.

It is quite beyond the scope of this work to enter into further details on the subject of the mixed fabrics, of which indeed there is a very large and yearly increasing variety. Among them we mention here only poplin as made in Ireland, a beautiful mixed fabric of linen, wool, and silk, and often woven in what is known as tartan pattern. Mixed woollen silk and cotton fabrics are very largely produced in this country as well as abroad.

Means of Distinguishing Silk from Wool and from Vegetable Fibres.

Owing to the manufacture of mixed fabrics, it has become a necessity to be enabled to detect and distinguish silk from woollen as well as from cotton and linen fibres. Microscopical investigation aided by chemical tests are resorted to for this purpose.

The animal fibres (silk, wool, and alpaca), are at once distinguished from the vegetable (flax, hemp, cotton), by the fact that the former are soluble in caustic potash, and the latter not. The animal fibres on being singed give off a smell of burnt feathers, and when ignited in the flame of a candle are almost immediately extinguished, a carbonaceous residue being left. Cotton and linen fibres continue to burn, do not give off the smell of burnt feathers, and do not leave a carbonaceous mass when extinguished. Wool and silk are coloured yellow by nitric acid (1·2 to 1·3 sp. gr.), cotton and linen not so. Nitrate of protoxide of mercury colours animal fibres intensely red, and upon the addition of a soluble alkaline sulphuret this colouration becomes black. Linen, or flax, and cotton are not at all acted upon by this reagent. An aqueous solution of picric acid dyes wool and silk intensely yellow, but not so vegetable fibres. The colourless liquid obtained (according to Liebermann) by boiling a solution of fuchsine with caustic potash does not impart to a mixed fabric of wool and cotton any colour at all; but when the fabric is thoroughly washed in water, the woollen fibre becomes intensely red-coloured, while the cotton fibre remains colourless. A solution of ammoniacal oxide of copper in excess of ammonia dissolves, first silk, next cotton, but not wool. When wool and floret silk are mixed the latter may be dissolved by successive treatment with nitric acid and ammonia, while wool is left. A solution of oxide of lead in caustic potash or soda may serve to distinguish wool from silk, owing to the fact that, in consequence of the former containing sulphur and the latter not, the mixture, when wool is present, becomes black. Nitro-prusside of sodium is undoubtedly the most delicate test for distinguishing between silk and wool in solution in caustic alkali, because, owing to the sulphur of the wool, this reagent produces in the solution a violet colouration.

By the aid of the microscope, cotton, wool, and silk are readily distinguished from each other. As for cotton (see p. 343), it has been fully described, and its microscopical appearance illustrated by woodcuts, as also have silk and woollen fibres. Of the latter we may now state that, whereas cotton fibre consists of only one cell, wool (as also hair and alpaca), is made up of numerous juxtaposed cells; the silk fibre being similar to the secreted matter of spiders and other kinds of caterpillars. The silk fibre (Fig. 253) is smooth, cylindrical, devoid of structure, not hollow inside, and equally broad. The surface is glossy and only seldom are any irregularities seen on it. If it is desired to detect in a woven fabric the genuineness of the silk, it is best to cut a sample to pieces, place it under water under the object-glass of a microscope magnifying 120 to 200 times, covering it with a thin piece of glass. (The round, glazed, equally proportioned silk fibre, Fig. 254, is easily distinguished from the unequal and scaled wool fibre (W in Fig. 255), and from the flat band-like and spiral cotton fibre (B, Fig. 255).) Under the microscope also the admixture of inferior with superior fibres of silk can be easily detected. A small microscope known as a "linen-prover" is sold for these examinations.

FIG. 253.

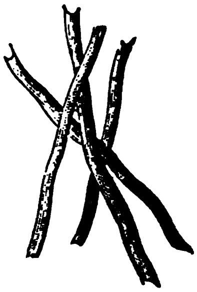


FIG. ~~450~~ 254

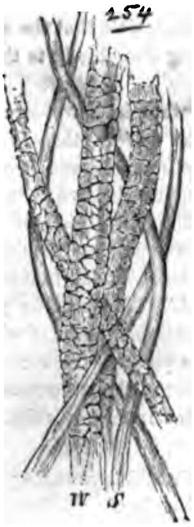
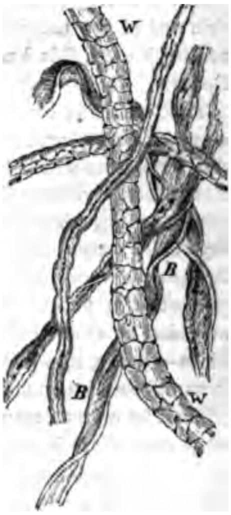


FIG. 255.



TANNING.

Tanning. The operation by which the skins of various animals, more especially those of the larger mammalia, are converted into leather is called tanning. By leather we understand a substance, tough, flexible, not harsh; further, distinguished by resisting putrefaction and by not yielding any glue when boiled in water, as is the case with tanned hide, sole leather, and the so-called red-tanned leather, or only after a very continued boiling, as with tawed skins of calves, sheep, or goats. Whatever the differences which obtain in the practical processes for carrying out the conversion, the physical principle involved is the same in all. Knapp's general definition of leather is that it is skin, in which by some means or other the agglutination of the fibres after drying has been prevented.

To a comparatively very recent period tanning was conducted on an empirical basis; it is only by a more accurate knowledge of the histological structure of the skin and of the tannin-containing materials that the real nature of the process has become known, this knowledge being due chiefly to the researches of F. Knapp and Rollet.

That which is converted into leather is, however, not the skin or hide, but really what is known anatomically as the *corium*, that is to say, the inner portion of the skins, from which by mechanical (cutting and scraping) as well as by chemical means (action of lime) the other integuments have been removed. In its most general sense tanning should:—1. Effect the prevention of putrefaction. 2. Render the dry skin a supple, fibrous, tough, non-transparent substance, and not horny as would be the case were the skin simply dried. A well-tanned skin or hide possessing these properties is termed "well finished." The specific process of tanning is of course preceded by some preliminary operations, the aim of which is to "dress" the skins or hides—that is, in scientific terms, to prepare the corium more or less perfectly free from all other integuments. Tanning in the more restricted sense of the word may be effected by a great many organic and inorganic substances; but in practice on the large scale there is employed:—

1. Tannin as contained in oak bark, producing brown-red tanned leather.
2. Alum and common salt—Tawing.
3. Fatty matters—Samian or Oil Tawing.

Anatomy of Animal Skin. Leaving the hair out of the question, the skin of the mammalia consists of several layers. The uppermost of these in which the hair is growing, the epidermis, is very thin, semi-transparent, and consists of cells which contain nuclei. This epidermis is covered by a more or less horny layer not possessing any vital properties, which gradually wears off, and is as gradually replaced by the *stratum Malpighii*, or Malphigian net, a structure consisting of cells containing fluid and nuclei. It is this layer in which the nerves and finer blood vessels are imbedded, together with the glands which provide the perspiration. In the tan-yards this layer is known as the *bloom side*, or hair side of the skin or hide. The real corium or derma, situated under the layer just mentioned, does not consist of cells, but is of a fibrous texture, and is that portion of the skin which after tanning constitutes the leather; in the living animal it is separated from the muscles by a more or less strongly developed fat-bearing tissue, the so-called *panniculus adiposus*, which is, however, removed in the dressing, the side of the skin or hide to which it was attached being termed the flesh side. All the histological constituents of skin or hide possess the property of swelling up when put into hot water, and of becoming after more or less protracted boiling converted into glue, more slowly when the skin is taken from old, more rapidly when from young animals. By the action of acetic acid the fibrous tissue of the skin is converted into a jelly-like transparent mass, in which the fibres are not only not destroyed but present with their peculiar structure. Alkaline leys dissolve this tissue but very slowly; while lime- and baryta-water have no other effect on it than simply the dissolving therefrom of the cellular binding tissue which permeates it, and which is an albumen compound also acted upon by dilute acids.

The various operations of tanning, more particularly the preliminary operations of steeping and dressing, are based upon the behaviour of the different histological elements of the skin and hide with alkaline and acid fluids; but the real process of tanning is based upon the behaviour of the corium with totally different reagents. This latter substance has the property of combining with tannic acid, several metallic oxides, viz., alumina, the oxides of iron and chromium, oxidised fatty matter, the insoluble metallic soaps (compounds of fat acids, viz., stearic, palmitinic acids, &c., with oxide of lead, &c.), picric acid, pinic acid (present in rosin), and other organic substances, somewhat in the same way as animal and vegetable fibre combine with dyes and pigments. In the most extended sense of the word all these substances are tanning agents, because they possess the property of being precipitated on and in the fibres of the corium, so that when the latter is dried the agglutination of the fibres is prevented, and the natural suppleness and softness of the skin preserved. But in the case of the application of alumina compounds, the softness is only imparted to the tanned skins by the operations of currying and dressing.

I. *Red- or Bark-Tanning.*

Tanning Materials.—This branch of industry employs as raw materials hides and vegetable materials containing tannin.

These vegetable materials contain essentially an astringent principle termed tannin or tannic acid, and which, though it differs in some of its properties as derived from different plants, agrees in being of an astringent taste, exhibiting acid reaction to test-paper, of yielding with salts of peroxide of iron a deep blue-black or green-black colour, of precipitating solutions of glue and cinchonine, and lastly of converting animal skins into leather. It has been proved that the tannin present in nut-galls—which, by-the-bye, are too expensive for use in tanning operations—is converted by the action of acids and by fermentation into glucose and gallic acid, the latter, however, not being suited for tanning purposes. Under the conditions which obtain during the tanning of hides, the tannic acid contained in oak bark (tan) cannot be split up similarly to nut-galls, and this negative property really aids the tanning operations greatly. All kinds of tannic acid are, when in contact with alkaline liquids, such as lime-water, caustic potassa, ammonia and with the simultaneous presence of air, decomposed and converted into brown coloured humin substances.

Oak Bark. This substance is for the tanner the most important of all tannin-containing materials, and cannot be replaced by any other. It is the inner bark of several kinds of oak, *Quercus robur*, *Q. pedunculata*, and is stripped from the trees and branches when these have attained an age of from nine to fifteen years, the bark when cut into splints being termed tan. According to E. Wolff, the quantity of tannin contained in oak-bark is as follows :—

	Tannic Acid.	Age of the Trees.
In the crude bark covered with the rind	10·86 per cent	41 to 53
,, inside layer of the old bark ...	14·43 ,,	41 to 53
,, inside of the bark	13·23 ,,	41 to 53
,, crude bark and inside of bark ...	11·69 ,,	41 to 53
,, inside layer and inside of bark	13·92 ,,	41 to 53
,, inside of bark	13·95 ,,	14 to 15
,, ,, ,, ...	15·83 ,,	2 to 7

According to Büchner's researches (1867) the quantity of tannic acid contained in the best kinds of oak bark does not exceed 6 to 7 per cent. The fir bark (produce of *Pinus sylvestris*) is one of the best tanning materials, and is frequently used for sole leather; this bark is stripped off the trees immediately after they have been cut down for timber. While J. Feser found 5 to 15 per cent of tannin in this bark, Dr. Wagner found only 7·3 per cent. In the United States the bark of the *Abies canadensis* is used; and an extract is in the trade, which according to Nessler's researches (1867) contains 14·3 per cent of tannic acid. The extract is imported into this country under the erroneous appellation of hemlock extract. The bark of the elm with 3 to 4 per cent tannin, the bark of the horse-chestnut with about 2 per cent tannin, and beech-tree bark with also about 2 per cent tannin, are all employed for tanning purposes. The younger branches and twigs of the willow trees yield a bark (3 to 5 per cent tannin) which is especially suited for certain kinds of glove leather; while another kind of willow bark is used for the tanning of Russian leather. In Tasmania and New South Wales the barks of some species of acacia, viz., *Acacia dealbata*, *A. melanoxylon*, *A. lasiophylla*, and *A. decurrens* are used. Among the native European plants which might be advantageously cultivated for tanning purposes, the *Polygonum bistorta* deserves to be mentioned: this plant should contain according to Fraas from 17 to 21 per cent (?) of tannic acid.

Sumac. This substance is, next to oak bark, one of the most important tanning materials; it is the product—the leaves and stems—of a shrub, the so-called tanner's sumac (*Rhus coriaria* and *R. typhina*), which grows wild in Southern Europe and the Levant, and is cultivated in North America and Algeria. The shoots from the roots are collected and planted in June, and after some three years' growth, the shrubs are large enough to admit of the branches and leaves being gathered. The young branches and twigs are cut off, and after drying in the sun, the leaves are beaten off with sticks or clubs, and next crushed under mill-stones, sifted, and packed into sacks, and thus sent into the market. The sumac of commerce is a coarse powder, exhibiting a yellow or blue-green colour, and containing 12 to 16·5 per cent of tannic acid. By keeping, the tannic acid of sumac is converted into secondary products, owing to a spontaneous fermentation. Sumac also contains a yellow dye-stuff which seems to be identical with quercitrin. With sumac should not be confused another material of the same name, but distinguished as Italian or Venetian sumac, and derived from the *Rhuscotinus*, also yielding fustic or yellow dye-wood. Italian sumac is the pulverised bark of the young twigs and leaves of this plant, which under the name of ruga grows in Southern Europe and also near Vienna; it is largely used in the countries where it grows for tanning purposes, being more particularly employed for preparing goat- and sheep-skins.

Dividivi. The material designated by this name is the seed capsule of some trees found native in Central America, and belonging to the *Cæsalpiniaciæ;* these seed capsules are about 6 centims. long, are bent as an S, have a brown-red colour, and contain olive-green coloured, egg-shaped, polished seeds. In 1768 the Spaniards brought this material to Europe, where it is used for tanning purposes on account of the tannin contained in the epidermis of the capsules (more correctly *siliquæ*, or pods). The quantity of tannin was found by Müller to be 49 per cent, by Fleck 32·4 per cent, while Dr. Wagner found from 19 to 26·7 per cent. Dividivi is rather an expensive tanning material, but is occasionally used for dyeing purposes. Among the tannin-containing substances which are occasionally imported from abroad may be mentioned the bablah, the produce of the *Acacia Bablah* and allied species. This material contains, according to Fleck, 20·5 per cent tannin, while Dr. Wagner found 14·5 per cent. Algarobilla, the seed capsules of the *Prosopis pallida*, a native of Chili, has been also occasionally employed as tanning material in this country. Although myrobolans, the fruits of *Terminalia citra*, *T. Bellirica*, and *T. Chebula*, are imported from Bombay, they contain too little tannin to be of any service in tan-yards.

Nut Galls. We understand by this name an excrescence formed on the leaves of the *Quercus infectoria* by the puncture of the female insect of the *Cynips gallæ tinctoriæ*, or oak wasp, effected in the leaves and young twigs in order to deposit its eggs; the juices of the tree collect round the egg, and on hardening form the nut-gall. This material is best collected before the young insect has become fully developed, because then the gall contains the largest quantity of tannic acid. In the market three varieties are met with, termed black, green, and white galls. The black and green variety have been gathered before the insect became fully developed inside the nut; these galls therefore do not exhibit outwardly any hole or opening, but on breaking the gall there will be observed in the centre a small cavity surrounded by a light brown friable substance, which contains the larva of the insect. Galls are generally spherical, but exhibit small irregularities of surface, and are of a black-green or grey colour. The white galls are gathered after the insect is fully developed, and has by perforating the tissue of the gall escaped. This variety is more spongy, its colour is a red-brown or brown-yellow. Galls of good quality are obtained only from warmer countries, for although galls are formed in our climate upon oak leaves, the quantity of tannin contained amounts to only 3 to 5 per cent. Fehling found in Aleppo galls from 60 to 66 per cent of tannic acid, while Fleck found 58·71 per cent of this acid, and 5·9 per cent gallic acid.

Valonia Nuts. These are the dried immature acorn cups of two species of oak, *Quercus ægilops* and *Valonia camata*, both being employed in tanning as well as the valonia nuts produced by the puncture of the *Cynips quercus calycis*. The quantity of tannic acid met with in these substances averages about 40 to 45 per cent. In the so-called valonia flour, obtained by grinding the acorns belonging to this class, Dr. Wagner found 19 to 27 per cent of tannin. The acorn cups are imported under the name of *drillot*, and according to Rothe these contain 43 to 45 per cent of tannin.

Chinese Galls. Under this name has been known in the trade since 1847, and imported from Japan, China, and Nepaul, the excrescence upon a kind of sumac, *Rhus javanica* and *R. semialata*, produced by the puncture of the *Aphis sinensis*. This gall-nut is rather oblong or bean-shaped, with an irregular surface covered with a yellow-grey felt; the length varies from 3 to 10 centims., and the thickness from 1·5 to 4 centims.; the texture is horny; the quantity of tannin varies from 60 to 70 per cent.

Cutch. The substances long known in medicine under the name of catechu and kino have been for the last fifty years also employed as tanning materials. Theyare vegetable extracts, that known as cutch (trade term) being obtained by exhausting with boiling water the pith of the wood of the *Acacia catechu*, a tree met with in different parts of the tropical regions of Asia. The liquor obtained by boiling the pith-wood in water is inspissated, and on cooling forms a solid mass, which is brought into commerce in various shapes and named after the port of shipment. Bombay cutch is met with in the shape of large square blocks, through and round which the leaves of a kind of palm-tree are placed. The colour of the fracture of this substance is a brown-black with a fatty gloss; externally the mass is dull and friable. Bengal cutch is prepared from the nuts of the *Areca catechu*, and occurs in commerce as large, irregularly-shaped cakes, externally brown, internally more yellow-coloured. Gambir is a variety of cutch prepared in Sumatra, Singapore, and Malacca, and especially in the Island of Riouw, from the leaves and stems of the *Uncaria Gambir*. The dry extract occurs in commerce in small cubical blocks, which are light, of a cinnamon-colour, and very friable, the fracture being earthy. All these substances contain about 40 to 50 per cent of a peculiar kind of tannic acid or catechu-tannic acid, the formula of which, according to J. Löwe, is $C_{15}H_{14}O_6$, as well as a peculiar acid, catechutic acid, $C_{16}H_{14}O_6$, not of much use in the tanning process.

Kino. This drug is very similar to catechu, and is said to be the extract prepared from various plants, viz.:—

African kino from	*Pterocarpus erinaceus*,
East Indian kino from	*Pterocarpus Marsupium*,
East Indian kino, according to others, from	*Butea frondosa*,
West Indian kino from	*Coccolaba uvifera*,
Australian kino from	*Eucalyptus resinifera*.

Kino is met with in small, angular, brittle, brown-red to black-coloured masses, the powder of which is always brown-red. It is soluble in hot water and alcohol, yielding a blood-red solution of an astringent and sweet taste. Kino contains from 30 to 40 per cent of a tannic acid similar to that contained in cutch; both of these materials are especially useful in so-called quick tanning.

Estimation of the Value of the Tanning Materials. The value of all the tanning materials entirely depends upon the quantity of tannic acid they contain. The latter is soluble in water, and more or less completely precipitated from that solution by various reagents, such as glue and animal skin, acetate of copper, acetate of oxide of iron, cinchonine and quinine, while a solution of permanganate of potash completely destroys the tannic acid. Upon these properties the following properties have been based for the approximative estimation of the quantity of tannic acid present in various tanning materials:—

1. Precipitation by glue or skin:—
    - *a.* Weighing of the skin before and after immersion in the liquor containing tannin, the increase of weight giving the quantity of tannic acid.—(Davy).
    - *b.* Precipitation with gelatine solution of known strength.—(Fehling).
    - *c.* Titration by means of an aluminated solution of glue.—(G. Müller).
    - *d.* First determine the specific gravity of the tannin solution by means of an areometer, next remove the tannin by skin, and then again take specific gravity of liquid, the decrease being proportionate to the quantity of tannin in the original liquor.—(C. Hammer).

2. Precipitation of tannin by acetate of copper, and estimation of the relation between tannin and oxide of copper in the precipitate:—
   - *a.* Volumetrically.—(H. Fleck); or
   - *b.* By the gravimetrical method.—(E. Wolff).
3. Volumetrical estimation of tannin by acetate of iron.—(R. Handtke).
4. Oxidation of tannic acid by permanganate of potash.—(Löwenthal).
5. Precipitation of tannin by means of cinchonin, the solution of which is tinged red by means of fuchsin. 1 grm. of quercitannic acid requires 0·7315 grm. cinchonine, equal to 4·523 grms. of crystallised neutral sulphate of cinchonin.—(R. Wagner).

The Skins. The skins of almost all quadrupeds might be converted into leather by tanning; but the tanner chiefly prepares his leather from the hides of cattle, occasionally from the hides of horses and asses as well as of pigs. The quality of the hides not only depends upon the kind of animal, but also upon its fodder and mode of living, The hides of wild cattle yield a more compact and stronger leather than the hides of our domesticated beasts; among these the stall-fed have better hides than the meadow-fed or grazing cattle. The thickness of the hide varies considerably on different parts of the body, the thickest part being near the head and the middle of the back, while at the belly the hide is thinnest. These differences are less conspicuous in sheep, goats, and calves. As regards sheep it would appear that their skin is generally thinnest where their wool is longest.

The hides of bulls and oxen yield the best and stoutest leather for soles. In the raw—untanned—state, and with the hair still on, the hides are termed "green" or "fresh." Fresh or green hides are supplied to the tanners by the butchers, or are imported either dry or salted. A hide weighing in fresh state from 25 to 30 kilos. loses by drying more than half its weight. South America (Bahia, Buenos Ayres, &c.) exports a large quantity of hides, both dry as well as salted and cured by smoking. The hides of cows yield generally an inferior grained leather; but South American cow hides may be worked for light sole leather. Calves' hides, again, are thinner, but when well tanned, curried, and dressed, yield a very soft and supple upper leather for boots and shoes. Horse hides are only tanned for saddlery purposes, while sheep- and goat-skins and the skins of lambs are tanned—or more generally tawed—for the purpose of making wash-leather, maraquin, glove-leather, bookbinders'-leather. Pigs' hides and seals' skins are tanned for saddlery purposes.

The Several Operations. The several operations of the oak bark tanning process may be reduced to three, viz.:—A. The cleansing and dressing of the hide on the hair and flesh side; in other terms, the separation of the corium from the other integuments. B. The true tanning. C. The currying and dressing operation, by which the tanned hide becomes a saleable article. These three operations are again subdivided as follows:—

A. The cleansing of the hide:—

1. Steeping and macerating the hide.
2. Dressing the flesh side.
3. Dressing the hair side.
4. The swelling of the cleansed hide.

B. The tanning of the cleansed hide, performed either by placing it in tanks or pits with oak bark and water, or in a liquor of these previously prepared, or by the so-called quick method.

C. The dressing and currying of the tanned hides, by which is understood all the operations which tend to improve the compactness of texture, or give a better grain and better appearance to the leather, together with softness, toughness, suppleness and colour.

Cleansing the Hides. A. This operation includes:—1. The steeping or macerating of the hide in water for the purpose of rendering the texture uniformly soft and so supple that it may be bent without danger of cracking, while, on the other hand, this steeping also effects a cleansing of the hide by removing from it blood and dirt. The fresh hides of recently slaughtered animals require a maceration in water for some two or three days, but dried, cured, or salted hides have to be left macerating for some eight to ten days. This operation should, if possible, be carried on in a stream of water; but if there is no convenience, then the hides are placed in large tanks; in either case the hides are taken out twice daily and put back into the water again.

Cleansing of the Flesh Side. When the hides have become quite soft, they are—(2) cleansed or dressed on the flesh side by being placed with the hair side downwards on a "tree," a stout semi-circular plank, one end of which is placed on the ground while the other is supported by a trestle, so that the plank is in a sloping position. The workman has a so-called dressing-knife, a tool to which handles are fastened, and which is bent so as to form a slight curve; with this knife he shaves, or, as it were, planes off, from the hide all fatty tissue and integuments which are situated between the hide and the muscles. At the same time the water is squeezed out of the hide to some extent.

After a preliminary or first dressing, the hides are again placed for twenty-four hours in water; the dressing and planing is then quite finished, and the hides having been well washed, are left to drain on the tree ready for removing the hair. In some instances the hides are washed by the aid of "possing-sticks," and "fulled" by means of machinery, by which the operation is greatly shortened, so much so, that two to three days suffice, instead of, as is usual by the aid of manual labour, eight to ten days.

Cleansing the Hair Side. 3. This operation aims at the removal from the corium of the epidermis and hair-containing integuments. As the hair and integuments connected therewith are very firmly attached to the corium, the removal can only be safely proceeded with, so as to leave the corium uninjured, by the employment of a menstruum which more or less dissolves and causes the epidermis to swell up. For this purpose the hides are usually placed in lime-pits, the effect of the lime being the partial dissociation (in an anatomical sense) of the epidermis, so that it and the hairs may be readily removed by mechanical means.

The effect is usually obtained by—*a*. Sweating; *b*. Liming; *c*. Application of rusma or compounds of sulphuret of calcium.

a. A semi-putrefactive fermentation called sweating is employed in the case of thick hides, such as serve for sole leather, which are not placed in lime owing to the fact that it cannot be completely removed, and would render the leather brittle. The operation of sweating consists in placing the hides one upon the other, the flesh side turned inward, some salt or crude wood vinegar having been first rubbed in, in a tank, or box, which can be closed so that the heat generated by the fermentation which sets in may be confined as much as possible to aid the action. As soon as the evolution of ammonia is perceptible, the hides are ready for the removal of the hair, which is shaved off, together with the epidermis, by the aid of the dressing-knife.

Instead of causing the sweating to be done by fermentation, the hides are sometimes hung on laths in rooms either heated by means of steam or by fire. A temperature of 30° to 50° should be kept up, together with a good current of steam, by which the epidermis is thoroughly softened. In order to prevent any injury to the corium, the hides are sometimes submitted to what may be termed a cold sweating process, consisting essentially in placing the hides in water-tight tanks, in which there is a constant current of fresh water, the temperature being kept at 6° to 12°. The hides thus submitted to a constantly moist atmosphere become, after six to twelve days, without any perceptible putrefaction, fitted for the removal of the epidermis and hair.

b. The liming of the hides not only prepares them for the removal of the hair, but also saponifies the fatty matter; and though the lime soap thus formed is insoluble in water, it is removed by subsequent mechanical and chemical operations. The operation of liming is carried on in pits, into which, along with milk of lime, the hides are placed so as to be quite covered. Usually several (three to five) pits are in use at once, each of which contains a different quantity of lime. That the milk of lime should be frequently stirred in these pits is of course evident. The hides remain in the lime-pits for three to four weeks.

c. The very thin skins of the smaller animals will neither sustain sweating nor liming and are therefore treated with rusma, a salve-like mixture of orpiment, 1 part with 2 to 3 parts of slaked lime. By the rubbing in of this mixture on the hair side of the skins, the hairs are so softened as to make their removal an easy matter. Böttger states that hydrosulphuret of calcium has the same effect; hence the lime of the purifiers of the gas-works has been of late years frequently employed for treating hides as well as skins, with the additional advantage of yielding a better leather.

Stripping off the Hair. As soon as the hides are sufficiently prepared to admit of the removal of the hair and epidermis, they are stretched out on the tree and the integuments peeled off by the aid of the blunt dressing-knife. In order to give to the dressing-knife a better grip, the workman strews some fine sand on the hide, and if he has to deal with very heavy and thick hides, uses a large and rather sharp knife. When the hair and the epidermis have been removed, the hides are again washed and macerated in water, and after this dressed; that is to say, reduced as much as possible to an equal thickness, while the waste—tail, leg, and head pieces—are cut off and the hide planed, thereby losing some 10 to 12 per cent in weight.

Swelling the Hides. The aim of this operation is to remove the lime, and also to render the corium more capable of readily absorbing the tan materials. This end is attained by placing the hides in a so-called sour bath, made of refuse malt and bran, which by acid fermentation yields as active principles propionic, lactic, and butyric acids.

The lime is removed from the dressed hides when placed in this acid liquid, and the lime-soap present becoming decomposed, the fatty acids thus set free float on the surface of the liquid. The soluble lime salts are completely removed from the hides by a subsequent thorough washing with water. The thickness of the hides is doubled by the swelling action of the acid liquid, aided by the mechanical action of the carbonic acid evolved from the carbonate of lime deposited within the fibres of the hides; while the butyric acid fermentation distends the fibres of the hides by the gases thereby evolved. When the hides have not been treated with lime but have been submitted to a "sweating," they do not require the acid bath, but are simply placed in water for the purpose of swelling them. Yet the sour bath is preferable owing to its more regular action.

Instead of using the preceding mixture for the purposes of removing the lime and of swelling the hides, they are often placed in acid tan liquor (red tan liquor), that is to say, a liquor containing exhausted oak bark solution which has served for tanning; this liquor appears to contain also large quantities of lactic and butyric acids. The dressed hides are first placed in a diluted red liquor and then in a stronger liquor, this operation taking some 12 to 14 days. Macbride and Seguin have proposed to substitute very dilute sulphuric acid (1 in 1500), but although by the use of this acid the operation of swelling is rendered far more rapid, the quality of the leather is impaired. Phosphates and animal excreta which contain a large quantity of uric acid, such as that of dogs and of pigeons, have been, and in many cases are still, used for the purpose of swelling hides, especially skins of sheep, calves, and goats.

The Tanning. B. The main object of the operations just described is first to obtain the corium as much as possible separated from the other integuments and textures belonging to the skin, and next to render the corium as much as possible permeable by the liquor in which the tannin-containing vegetable matter is dissolved. In practice it is taken for granted that a dry hide gains one-third in weight by being converted into leather, consequently it absorbs that quantity of tannin.

The impregnation of the fibres of the hide or skin with tannin is effected by two different methods, viz.:—

1. By placing the hides between layers of oak bark chips in a tank, so-called tanning in the bark; or

2. By immersing the hides, first in a dilute, and again in a concentrated aqueous infusion of oak bark.

Tanning in the Bark. 1. This mode of tanning is at the present time confined to heavy hides intended for sole leather. The tanks in which this operation is carried on are made of wood, either oak or fir, are of course watertight, and are usually sunk into the soil. Brick cisterns lined with cement are occasionally used, but are objectionable, at least when recently built, on account of the deteriorating action of the lime and cement upon the oak bark. In some parts of Germany tanks constructed of slabs of slate or sandstone are used. Each tank has sufficient capacity to contain 50 to 60 hides. On the bottom of the tank is first placed a layer of exhausted (spent) tan, and upon this a layer of some 3 centimetres in thickness of fresh bark, then a hide with the hair side downwards, again a layer of fresh oak bark, and again a hide, alternately until the tank is nearly filled, care being taken to put some more bark on the thickest part of the hides, and to fill not only all interstices with bark, but to put on the top a layer of some 30 centimetres thickness of spent tan. Water is next poured into the tank until it stands a few centimetres above the topmost hide; this having been done, a lid—in England loose planks—is placed on the tank, the contents of which are left undisturbed for some time. When Valonia flour is employed with the oak bark only half the quantity of the latter is necessary.

The hides are left in "the first bark" for 8 to 10 weeks, the period being a little shortened if Valonia flour is also used. Before all the tannin has been absorbed, and as a consequence the formation of volatile and odorous acids (valerianic, butyric, &c.), has commenced, the hides are transferred to another tank and again placed between alternate layers of fresh bark, the only difference in the arrangement being that the hides which were first placed on the top are now laid at the bottom of the tank. The hides are now left for three to four months, so as to thoroughly absorb the tannin. They are next placed for some four to five months in another tank which contains less bark. In the case of very heavy and thick hides the process is repeated four or even five and six times. The quantity of bark required for obtaining thoroughly well-tanned leather depends partly on the quality of the bark, and somewhat on the condition of the hides. Usually the tanners reckon that the quantity of bark required amounts to four to six times the weight of the dry hides; and taking the weight of these at an average of 20 kilos.—

For the first tank there will be required	40	kilos. of bark.
,, second ,, ,, ,,	35	,,
,, third ,, ,, ,,	30	,,
	105	kilos. of bark.

A dried and well-tanned hide weighs about 22 kilos., or 10 to 12 per cent more than the dry raw hide. A thoroughly tanned hide exhibits when cut with a sharp knife a uniform texture free from fleshy or horny portions, while the grain on the hair side should not on being bent slowly exhibit signs of cracking.

Tanning in Liquor. 2. The thinner hides, and indeed most skins (when tanned, as distinguished from tawing), are placed in infusions of the tannin-containing material. There are various methods in use for this operation, which is based mainly upon a thorough uniform swelling of the hides, so that when these are placed in weak liquors the tannin may penetrate readily and uniformly. The hides are, in fact, very gradually tanned. When taken from a liquor the fluid is forced by mechanical means out of the hides before they are placed in a stronger liquor, this liquor being obtained by exhausting the tanning materials by the aid of cold water. The thinner kinds of hides are thoroughly tanned in seven to eight, the heavier hides in eleven to thirteen weeks.

Quick Tanning. Many methods—some quite impracticable and most of them thoroughly irrational—have been proposed for converting hides into leather in a very short time. Of these different methods we briefly mention the following:—1. The hide is simply placed in an infusion of the tannin-containing material—Macbride's process, improved by Seguin (1792). Application of hydrostatic pressure to force the liquor through the hides, kept from contact with each other by a stout woollen tissue. 2. Circulation of the tannin-containing fluid, several tanks being connected together by means of pipes, and the liquor being forced through the tanks by means of pumps (Ogereau, Sterlingue, and Turnbull's methods. 3. The hides are sewn together so as to form sacks, which are filled with oak bark chips and water and then placed in an aqueous solution of cutch, to which, in order to increase its specific gravity, coarse molasses is added—Turnbull's method by increased endosmose. At the time this mode of proceeding was brought forward, the diffusion of liquids by dialysis (discovered by Graham in 1861) was unknown. 4. Motion of the hides in the tannin-containing liquids, the hides being placed in a cylinder constructed of wooden laths so as to leave open spaces between them. This cylinder is immersed horizontally in the liquid to a greater or less depth, so that in every revolution the hides are alternately in and out of the liquid—Brown, Squire, and C. Knoderer's methods. 5. Application of mechanical pressure to the hides.

which having been from time to time removed from the tanning tanks, are placed upon perforated planks, and either pressed under a heavy roller or are placed in a press—Jones, Nossiter, Cox, and Herapath's method. 6. Application of hydrostatic pressure for the purpose of causing the tan-liquor to penetrate the hides, which are sewn together so as to form bags, which having been filled with oak bark liquor, are placed in suitably constructed vessels, so that hydraulic pressure may be applied without fear of bursting the bags; or the hides are fastened by means of screws and bolts, placed in a framework which is immersed in a well-constructed cistern filled with tan-liquor, hydraulic pressure being applied—Drake, Chaplin, and Sautelet's methods. 7. Snyder's method of punctation, consisting in perforating the hide over its whole surface, the punctation being effected by sharp needles, so as to constitute artificial pores. The experiments of Knapp have proved the thorough irrationality of this plan, it having been found that the hide is so permeable to tannin-liquor that a piece of calf-skin when placed in a solution of tannin of the consistency of syrup is thoroughly well tanned in about an hour's time. 8. Application of a vacuum by placing the hides in a vessel from which the air may be withdrawn by the aid of air-pumps; tan-liquor having been forced into the vessel, the air is re-admitted and again withdrawn—Knowly and Knewsbury's plan. Knoderer has recently found that by a judicious combination of the vacuum method, followed by motion and fulling of the hides in the tan-liquor, the operation of tanning is much shortened. The reader should bear in mind that the methods here alluded to are not now in general use.

Dressing or Currying the Leather. When the hides have been converted into leather by the processes described, they are not by any means fit for use nor ready for sale as a finished material, but require to be dressed, or, as it is technically termed, curried, an operation not necessarily performed by the tanner—at least, never so in England and France. The several operations are not similar for all kinds of leather, but depend to some extent upon the use to which it is intended to be put. For instance, sole leather is submitted simply to a process the object of which is to render it sufficiently stiff and compact, so as not to alter its shape by wear.

Sole Leather. The dressing or currying of this kind of leather consists mainly in submitting it to a mechanical operation of hammering, by which the material is rendered more compact. As soon, therefore, as the hides are taken from the tanning tanks, the adhering spent tan is brushed off with a broom, after which the hide is dried in a cool place, and when dry laid flat upon a polished stone slab, and then beaten with wooden or iron hammers, an operation in large establishments performed by hammers moved by machinery.

Upper Leather. The dressing of this kind of leather, chiefly used by sadlers and boot and shoe makers, is a far more complicated process, and depends in a great measure on the use for which the leather is intended. The first of these operations is

The Paring. the paring or whitening, which means the cutting away, by the aid of a tanner's shaving-knife, of all portions of the hide which are too thick, so that the whole hide may be made of uniform thickness. This operation is carried on upon the tanner's "wooden leg," the hide being placed with the hair-side downwards. When goat, lamb, sheep, or calf-skins are to be pared, they are placed on a polished slab of marble, and having been well stretched, the raw or projecting parts are cut off with the tanner's shaving-knife.

The Scraping or Smoothing. The aim of this operation is similar to that of the former, and more particularly is employed in the case of leather intended for making gloves. The leather is first dried and next fixed on the "perching-stick," one end of the skin remaining free, the other being taken hold of by the operator with a pair of forceps. The skin having been stretched, the perching-knife, a highly polished somewhat convex steel disc of 18 to 30 centims. diameter, and provided in the centre with an opening fitted with a piece of leather serving as a handle, is brought into use, the portions of the skin which require to be pared off being usually indicated by being rubbed over with chalk.

Graining the Leather. As in consequence of the drying of the leather the grain has become flat, smooth, and unequal, it is raised by an operation performed by means of the pommel, also termed the graining- or crimping-board, a piece of hard wood 30 centims. in length by 10 to 12 centims. breadth, flat and smooth on the top, but on the opposite side, in the direction of the length, somewhat curved, so that it is thickest in the middle, this part being provided with parallel notches, which are occasionally sharpened by means of a file; a leather strap is fastened to the top as a handle. The leather to be grained, having been placed on the dressing-table, is fastened to the edge of the wooden board by means of iron clamps, and those portions of the leather, the grain of which has to be raised, having been somewhat bent, are rubbed with the pommel so as to render the grain uniformly visible,

Polishing with Pumice-Stone. Such kinds of leather as require no grain (for instance, the leather used in carding machines) after having been pared, are moistened and then rubbed over on both sides with pumice-stone, being thus rendered smooth; while leather which requires a higher gloss, such as the coloured leathers, are treated with **Raising the Grain Slightly with Pommels of Cork.** a pommel made of cork, by which the leather is caused to assume a velvety appearance. Again, if a still higher gloss is required, the leather **Smoothing with the Tawer's Softening Iron.** is first smoothed, or rather ironed, with iron or copper "sleekers," and next polished with glass sleekers, a stout cylindrical piece of glass, 0·3 metre in length by 10 centims. diameter, the leather being placed on a tanner's **Rolling.** wooden-leg. Leather intended for saddles, in order to impart to it the appearance natural to hog's leather, is passed through rollers, the surfaces of which are provided with blunt points, which, being forced into the leather, give to it the desired appearance.

Finishing Off. In order to remove from the leather any creases and other inequalities of surface, it is damped, and then smoothed with a flattening-iron, or, if the skins are thin, with a piece of horn provided with blunt teeth.

Greasing. When the upper leather is required to be very supple and soft, it is greased; that is to say, it is rubbed with a mixture of fish-oil and tallow, or better, with the peculiarly modified fish-oil which has been used in "chamoising," having been recovered by the aid of a solution of potash from the chamois leather skins. The hides to be greased are first moistened, and having been rubbed with the greasy matter, are dried in heated rooms, so that the fatty materials, by actually combining with the hides, become, as it were, tanned and tawed at the same time. The greasing is therefore not simply an operation of dressing, but in reality a second tanning (technically tawing) process.

The black colour usually seen on the surface of leather required for saddlery and boot-making is imparted to the hides by rubbing them with a fresh solution of oak bark and then sponging them over with a solution of copperas to which some blue vitriol has been added; the hides are then again dressed, and lastly rubbed with a paste made of fish-oil, tallow, lamp-black, yellow wax, soap, and copperas, the object of this operation being to protect the leather from the injurious effects of the shoe-blacking, which usually contains sulphuric acid. (For a shoe-blacking without acid see "Chemical News," vol. xxiv., p. 120). Finally, the leather is painted or brushed over with a mixed tallow and glue solution, and then, having been polished again with glass, is ready for sale. In order to keep leather supple and soft, it is best to rub it with a mixture of fish-oil and lard.

Yufts, Russia Leather. Under the name of yufts is understood a peculiar kind of leather, usually of a red or black colour, which is very water-tight and strong. This kind of leather used to be made exclusively in Russia, whence it is obtained in large quantity, the name being derived from the Russian *Jufti*, signifying a pair, and apparently due to the fact that in tanning the hides are sewed together in pairs. The hides usually prepared for Russia leather are those of young cattle; sometimes, however, the hides of horses and the skins of sheep, goats, and calves are employed. The operations for preparing yufti are :—1. The cleansing of the hides, performed in the usual manner with lime. 2. The swelling of the hides in an acid-bath prepared with malt, exhausted tan-liquor, or with kaschka (excreta of dogs rubbed up with water). 3. The tanning, not performed with oak bark, but with the barks of various kinds of willows, fir and birch bark also being used. The dressed hides are first placed for some days in partly exhausted bark, and are then put into the tanning tanks along with bark (as above described), or are sometimes placed in a warm infusion of the tannin-containing materials. The tanning continues for five to six weeks. 4. The tanned hides are placed on the planing-block for the purpose of draining, and are next impregnated with *diggut* or *eiachert*, oil of birch, obtained by a process of dry distillation from birch wood. This oil contains creosote, phenol (of a peculiar kind according to Louginine), and paraffin. It is rubbed into the hides on the flesh side, and when thoroughly impregnated they are stretched until they become soft and supple. The hides are next rubbed on the hair side with a solution of alum, and then grained and dried. The dry hides are dyed in pairs, sewn together so as to form a sack, into which a decoction of dye material is poured. When a red colour is desired, the dye is prepared from sandal wood, there being added to the former lime-water, to the latter some potash or soda. In more recent methods the hides are dyed by being brushed over five or six times with the dye material. The dry leather is finally dressed by the mechanical operations previously described. The use of yufts for book-binding and other purposes is well known. Owing to the empyreumatic oil with which this kind of leather is impregnated insects do not attack it.

Morocco Leather. By morocco leather is understood a kind of leather which, when genuine, is obtained from goat or kid skins, is very soft, elastic, highly coloured, and not lacquered. We distinguish between *genuine* morocco and the imitation obtained by the splitting of calf, sheep, and other skins, as chiefly employed in book-binding.

The preparing of morocco leather is undoubtedly one of the many industrial discoveries of the Saracens; even at the present day a great deal of morocco leather is made by their descendants in Northern Africa and in the Levant. The preparation of good morocco leather requires very great care, and especially as regards the preliminary operations. The skins are deprived of the hair by the aid of lime and sweating. The tanning material in general use is sumac, the skins being sewn up so as to form sacks into which water is poured together with pulverised sumac; by this mode of employing the tanning matter the operation is finished in three days. Calf and sheep skin are very generally tanned in England by the same method. The dyeing of morocco leather is not performed in the Oriental countries; the dry tanned skins are exported under the name of Meschin leather (*cuir en croutes*) to be dyed and dressed in Europe.

Dressing Morocco Leather. The skins are dyed and next dressed. The dyeing is performed—(α) by means of the dye-vat (for genuine morocco), or (β) with the brush (for imitation morocco). α. The operation of dyeing with the vat is performed in a small trough large enough to hold one skin, and filled with dye-liquor at 60° from a larger tank. The workman pours in no more of the dye material than can be conveniently absorbed by the skin, which is continually moved to and fro. The dyed skins are laid out flat, and from two to four dozen placed one upon the other. The dyeing operation is repeated several (three to five) times, care being taken to turn the heap over so that the undermost skin is placed on the top of the heap previous to beginning the dyeing operation again. The dyed skins are washed in water and next dressed. β. The imitation morocco is dyed by the dye-liquor being uniformly brushed over the skins; these having been first stretched on a table, the dye-liquor is brushed over more than once so as to produce a uniform hue. The effect of the dyeing is greatly enhanced by the dressing of the skins and the fine grain given to them. The dyed skins are first rubbed on the hair-side with linseed oil applied by means of a piece of flannel. The calendering or glazing by machinery is the next operation, after which the peculiar appearance of the surface is imparted by means of strong pressure or so-called platting. Yellow skins are not glazed, because their colour would thereby become a brown. The aniline colours are now largely employed in dyeing skins.

Cordwain, Cordovan Leather. This differs from morocco only by being prepared from heavy skins, and by retaining its natural grain or not being platted. It is usually met with dyed red, yellow, or black.

Lacquered Leather. This kind of leather, now largely used by coach-builders and for making shoes, boots, helmets and other military accoutrements, is an invention of the present time, its great merit being its property of resisting water, and in being supple and soft, while the lacquer, if well laid on, should not crack nor peel off. Only black lacquered leather is generally met with. On the tanned, rarely tawed, hide, which has not been greased, is very uniformly laid a varnish, which is thick and tough while cold but thinly fluid when warm; this having been done, the hide is placed in a brick-built stove kept at 50°, where the varnish dries after having become so fluid as to run uniformly over the surface of the leather, which is placed quite horizontally. The coloured lacquers are generally more thinly fluid and are dried at a lower temperature. The hides chiefly used for lacquering are cow-hides; or a thin hide is obtained by splitting thick hides and lacquering them.

The leather in use by pianoforte-makers for covering the hammers is prepared by a process usually kept a trade secret. This kind of leather requires to be soft and very elastic. All that is known about the process of preparing this material is that it is obtained by tanning and tawing (chamoising) combined; the hair having been removed, but not the epidermis, the hide is first fulled in oil, then washed in ley, bleached in the sun, and next tanned in a tepid oak bark infusion. Danish leather is prepared by tanning sheep, goat, kid, and lamb skins with willow bark; such leather being chiefly used for gloves. It is distinguished by its strength, suppleness, and bright colour.

II. *Tawing.*

Tawing; Preparation of White Leather.

This mode of preparing leather is based upon the peculiar action of the salts of alumina upon skins, not hides generally.

Four modifications of tawing are known, viz.:—1. Common tawing. This operation extends only to thin skins, such as sheep and goat skin, &c., which are treated only with alum and common salt without the application of oil. 2. Hungarian tawing process. Heavier hides not treated with lime are tawed and next chamoised. Klemm's method of preparing fatty leather is somewhat similar to this treatment. 3. The French or Erlanger tawing method, by which the skins are prepared for glove-leather. 4. Tawing by the aid of insoluble soaps, according to Knapp's suggestion.

Common Tawing.

1. The tawer obtains sheep skin, or occasionally goat skin, either with the wool off or "in the wool," as the term runs, in the latter case greater care being required, because the value of the wool, which, by careful working may be obtained in good condition, refunds a considerable portion of the expense of the operation by its sale. The various operations of tawing are in a certain measure similar to those of tanning.

The steeping and planing is carried on as in the tanning process. The workman places ten skins on the planing-tree, and dresses each skin with the dressing-knife on the hair as well as on the flesh side; next the wool or hair is shaved off after the skins have been first treated with the lime; but when "in the wool" the skins are cleansed with thin lime-water, which is laid on the flesh side of the skin by a brush made of cow's-hair, so that the wool is not brought into contact with lime. The wool is removed, not by a planing-iron, but by means of a piece of wood somewhat sharpened. The wool having been removed, the skins are brushed over with a mixture of equal parts of lime and sifted ashes; next the head and leg strips of the skin are turned inside. Each skin is then folded together and beaten, in order to prevent the wool being touched by the lime. The skins are left in this condition for eight to ten days until the wool is loosened. The skins are next thoroughly washed on the flesh side as well as on the wool side in order to remove the lime and dirt; this having been done the wool is partly pulled off by the hands, partly removed by a blunt tool. The skins thus deprived of wool are placed in the lime-pit and further treated as just described. In order to remove the paste adhering to the skins they are, on being removed, placed in a tank, where, owing to the quantity of animal matter dissolved in the water, a fermentation has arisen accompanied by an evolution of ammonia. By the action of this alkali a large portion of the fatty matter contained in the skins is removed. After being taken from the lime-pit the skins are placed on the dresser's block, and some parts, such as the ears, skin of tail, portion of top part of chest, cut off and thrown aside for the glue-boiler. The skins are put over night to soak in water, and then again placed on the dressing-block in order to be planed with a blunt iron on both sides of the skin; this operation is repeated after the skins have been placed in a tank containing water, and while there thoroughly beaten with a heavy wooden "possing-stick" in order to remove lime. In the subsequent planing the lime and lime-soap are forced out, and any wool that has remained shaved off. In order to dissolve the last traces of lime the skins are placed in an acid-tank containing bran and water, in which by fermentation lactic and acetic acid have been formed. These acids convert the lime of the skins into soluble salts, while the process causes the swelling of the skins, which thus become better adapted to absorb the tanning materials. The skins remain in the sour-tank for two to three days. The tanning material consists for 1 dicker (= 10 skins) of an alum ley, containing 0·75 kilo. of alum, 0·30 kilo. of common salt dissolved in 22·5 litres of boiling water. 1 litre of this liquid is poured into a trough, and having become tepid, each skin is separately thoroughly washed with and soaked in it, and then put aside without being wrung out, the skins being placed one upon the other so as to form a heap. After lying thus for two or three days, the skins are wrung out and hung up to dry slowly by exposure to air.

As regards the theory of the action of the alum ley in the tawing operation, it was formerly believed that only the chloride of aluminium—formed by double decomposition between the constituents of the common salt and the sulphate of alumina of the alum (the alkaline sulphates being considered useless)—was active, and that a basic chloride of aluminium (aluminium oxychloride) combined with the skin, there being left in solution hydrochlorate of alumina. It was also known that acetate of alumina, if used instead of alum ley, was quite as active and yielded excellent results. The experiments made by Dr. Knapp, sen., with alum, acetate of alumina, and chloride of aluminium, have proved that no decomposition ensues when the aluminium salt is taken up by the skin, the quantity taken up being for the undermentioned salts as follows:—

Of alum	8·5 per cent
Of sulphate of alumina	27·9 „ „
Of chloride of aluminium	27·3 „ „
Of acetate of alumina...	23·3 „ „

The alumina salts do not, however, combine with skin under all conditions in the same quantity as just mentioned, as experience proves that the skins absorb more when placed in concentrated than when in dilute solutions. As regards the part played by the common salt in the preparation of the alum ley, the salt is not there simply to bring about the conversion of the alumina sulphate into chloride of aluminium (recent experiments made by Knapp in 1866 have proved that by employing 1 atom of potash alum and 3 atoms of common salt = 37 per cent, no mutual decomposition ensues), but the salt is in this process active by itself, partly aiding dialytically the action of the alum, partly owing to its property—possessed also by alcohol—of withdrawing from animal tissues the water they contain sufficiently to prevent the fibres to become glued together by the drying of the substance, thus promoting the formation of leather. The dry and tawed skins will be found to have become shrunken and stiff, having lost much of their suppleness and flexibility. In order to remedy these defects the skins previously damped with water are submitted to a mechanical operation, being placed on the convex side of a curved iron, and stretched by being drawn between this fixed iron and a movable steel plate, which is fitted closely upon the other. After having been thus softened, the skins are stretched on a frame for some time to become dry. When dry they are ready for sale, the leather thus obtained being largely used under the name of white-skins for the lining of boots and shoes.

Hungarian Tawing Process. 2. This process is distinguished from that just described, inasmuch as the heavy hides of oxen, buffaloes, cows, horses, &c., are made into leather for saddlery and other purposes, while sometimes also the skins of wild boars and of other animals are thus tawed for making flail strings. The raw hides are first soaked in water to remove blood and impurities. Next the hair is shaved off by means of a sharp knife. This operation performed, the hides are put into an alum ley, which for a hide weighing 25 kilos., consists of 3 kilos. of alum, 3 of common salt, and 20 litres of hot water. This liquor when tepid is poured into an elliptical tub in which the hide is placed.

One of the workmen then jumps into the tub and by moving the hide about with his feet soaks it thoroughly with the liquor, in which it is then left for at least eight days, the operation of treading with the feet being repeated. The hide is now taken from the tub and hung up to dry, and when dry is stretched and "fatted" in by the following method:—The hide is warmed by being held over a charcoal fire, and when warm is rubbed on the hair as well as on the flesh side with molten tallow, of which some 3 kilos. are used for every hide. When thirty hides have been thus treated, they are one by one again held and moved to and fro over the fire, and next hung up in the open air to dry. The tallow partly combines with the hide.

The hides thus prepared are converted into a leather of excellent quality, especially suited for the harness of horses and saddlery work of a more common kind, in which, as in that used for artillery horses, great strength is required. This leather is cheap on account of its being prepared in a short time.

Glove Leather. 3. The so-called Erlanger, or French tawing process, is employed only for the production of the glacé, or kid leather, used for making gloves and ball-room shoes. The hair side of the skins intended to be converted into this leather is left unchanged, while as regards wash-leather gloves which are treated (tanned) with fish oil the hair side is cut off. The skins intended to be converted into kid leather are treated with extraordinary care, and thus acquire in a very high degree all the good quality of alum-tanned (or rather tawed) leather. As these skins are often intended to remain white or are dyed with delicate colours, the greatest care is taken to prevent any injury, as, for instance, contact with oak wood or with iron while wet.

Two kinds of skins are employed for conversion into the better varieties of kid leather; one of these, the more expensive, being the skins of young goats, fed solely with milk, the other being lamb skin. Each of these skins yields on an average 2 pairs of gloves. The leather of which ladies' ball-room shoes are made is obtained from the hides of young calves (so-called calf-kid). The preliminary operations of preparing this leather are exactly similar to those already described for the ordinary white leather; but the tawing operations are quite different, the skins being put into a peculiar mixture, by which they are not only tawed, but simultaneously impregnated with a sufficient quantity of oil to render them soft and give suppleness. The mixture consists of a paste composed of wheaten flour, yolks of eggs, alum, common salt, and water. The flour by the gluten it contains aids the absorption of the alumina compound, and thus assists the real tawing. The starch does not enter into the composition of the skins, while the yolk of eggs acts by the oil it naturally contains in the state of emulsion, this oil giving to the kid leather that suppleness and softness which is so much esteemed in gloves. It appears that emulsions made with almond oil (the so-called sweet oil of almonds—a fixed oil), olive oil, fish oil, and even paraffin, may be advantageously substituted for yolk of eggs. The skins are thoroughly soaked and kneaded in this mixture, to which, in France, there is sometimes added 2 to 3 per cent of carbolic acid for the purpose of preventing the too strong heating of the skins when impregnated with the mixture and packed in heaps. The skins are next stretched by hand and dried as rapidly as possibly by exposure to air. Having been damped, a dozen of the skins are placed between linen cloths and trodden upon to render them soft. After this they are, one by one, planed, dried, and again planed. Either by rubbing with a heavy polished glass disc or by the *appreteur*, simultaneously with the application of some white of egg, or a solution of gum, or of fine soap, a gloss is given to the skins, the hair side of which is the right side or dyed side. The dyes are applied either by immersion or by brushing over the leather; the latter, or English method of dyeing skins, is more ordinarily practised.

According to Knapp's researches very good white kid leather is obtained by tawing the epidermis (blöss) from lamb or goat skins in a saturated solution of stearic acid in alcohol. The leather thus obtained is very soft, has a whiter colour than ordinary glacé leather, and a beautiful gloss.

Knapp's Leather. 4. The preparation of leather with the aid of insoluble soaps, introduced by Knapp, would appear to have become of some importance. The property possessed by oxide of iron of acting as a tanning material has been known for a long time, and in 1855 Mr. Belford took out a patent in this country for a mineral tan method, in which oxide of iron was used; but good leather did not result. The hides do not become really tanned by being immersed in solutions of such metallic salts, as those of the protoxide and peroxide of iron, oxides of zinc and chromium; for though the acidity of these solutions is reduced to a minimum without producing a permanent precipitate, and thereby the deleterious action of the acid upon the fibres of the hides decreased, and though a certain combination of the oxide and fibres takes place, no real leather is formed because the substance when finished is not fitted for contact with water, for then the so-called tanning is washed out. Knapp's process also is not really a tanning but a tawing operation, by which the skins are alternately immersed in a solution containing 3 to 5 per cent of soft soap, and then in a saline solution of oxide of iron, or of chromium, containing 5 per cent of the salt, from which an insoluble metallic soap is precipitated and impregnated with the fibres. After this operation has been several times repeated the hides or skins are washed in water and dried. Although the exterior colour of good sound leather may be imitated, the real qualities of leather are wanting. Knapp's process is not in use or is so entirely modified by substituting alum for metallic oxides that the skins are tawed by a combination of the preceding tawing processes and the oil-tawing process now to be described.

III. *Sämian or Oil-Tawing Process.*

Samian Tawing Process. By this name is understood a peculiar process by which the skins and hides of various animals, such as harts, deer, sheep, calves, oxen (for the white leather for military use as belts, &c.), are converted into so-called oil- or wash-leather. The tanning material is oil, fat, tallow, or fish oil, to which recently there has been added 4 to 7 per cent of carbolic acid. The leather thus obtained is chiefly used for making military breeches, socks, vests, gloves, braces, belts, surgical applications, and not in small quantity for washing glass and porcelain, owing to its softness. On this account wash-leather is also largely used by gold and silversmiths for polishing trinkets with rouge (very carefully prepared oxide of iron). The upper or exterior layer of the corium, which owing to its greater compactness does not possess the ductility and suppleness of the lower or interior layer, is in the skins intended to be converted into wash-leather entirely cut away, so that no hair and flesh side are taken into consideration. The cutting away of this layer greatly promotes the absorption of the oil, which by the joint action of air and heat yields a product which is a dry compound of fibre and oil, in which the latter physically has disappeared, inasmuch as the leather is not impervious to water. Wash-leather differs in this respect from oil or fat leather; still, on immersion in water, the skin does not glue together and shrink. Thin skins, such as those of goats and lambs, are not deprived of their hair side, because it would render them too thin for use.

The skins intended to be made into wash-leather are, as regards the first stage of the operation, treated exactly as described for the skins treated with alum, the only difference being that the hair is removed together with the hair side portion of the skins, which are next placed in a bran bath in order to remove the lime. After this the skins are stretched and conveyed to the fulling machine in order to become saturated with oil, for which purpose the skins are first laid on a table or bench and are rubbed with oil, the hair side being placed uppermost. This having been done they are made into clouts and placed under the stampers of a machine so as to thoroughly impregnate them with oil. From time to time the skins are taken from the trough and exposed to the air, then again rubbed with oil and put under the stampers until enough oil has been absorbed. By the repeated exposure to air the skins become dry, and oil (fish oil is chiefly used) absorbed; the exposure to air is continued until the surface of the skins appears quite dry. When the skins have an odour somewhat similar to that of horse-radish, and have lost their fleshy odour, they have absorbed a sufficient quantity of oil, while a portion of the oil has been somewhat changed and has entered into combination with the fibre, another portion only mechanically adhering to the pores of the skins. The next operation therefore aims at rendering the process of the combination of the oil with the skins more rapid by bringing about a fermentation attended with an elevation of temperature; this is effected by placing the skins in a warm room, heaping them together, and covering them with canvas to keep in the heat which is generated, care being taken to air the heap from time to time in order to prevent overheating and consequent deterioration of the skins. This operation of airing the skins is repeated until by the spontaneous heating they have acquired a yellow colour and the workmen know by experience that the oxidation of the oil is finished. A portion of the oil (estimated at about 50 per cent of the quantity originally employed) is left in the skins in uncombined state, and is removed by washing with a tepid solution of potash. From this liquor there separates on being left at rest a portion of fat termed *dégras*, and which, as already mentioned, is employed for the dressing of tanned hides. The skins having been thus deprived of the excess of oil are wrung out, dried, and next dressed, in order to restore to them their softness and suppleness partly lost in the drying. Cordovan or Turkey leather, is oil-tawed without the hair side having been first removed, while the flesh side is blackened in the usual way. This kind of leather is chiefly used for ladies' boots and shoes. According to Knapp, skins from which the hair has been first removed may be tawed by treating them alternately with a solution of soap and dilute acids, so that the fatty acids are precipitated into the fibre. After the tawing the skins thus treated should be thoroughly washed in water to remove all acid. As regards the constitution of the leather, commonly known as wash-leather, tawed with oil, nothing is definitely known, but it would appear that this process of tawing has some analogy to the process of imparting oil to calico intended for Turkey-red dyeing.

Parchment. The substance known as parchment is not really leather, because its fibres are neither tanned nor tawed, as proved by the fact that boiling water readily converts parchment into a superior kind of glue similar to isinglass, of course too expensive for joiners' use. Parchment is essentially the well-cleansed and carefully dried skins of hares, rabbits, and especially of calves and sheep.

Ordinary parchment is prepared from sheep-skins, but the variety known as vellum, *Vélin or Parchement vierge*, is far finer, and is made from the skins of young calves, goats, and stillborn lambs. According to the use intended to be made of parchment, so is its preparation modified. The skins are first soaked in water and then placed in the lime-pits. Sheep skins are cleansed by working with cream of lime in order to preserve the wool. When the hair has been removed the skins are washed, being placed on the dresser's block, and usually also planed with a sharp knife to remove the superfluous fleshy parts. This having been done, each skin is separately stretched in a frame, in a manner very similar to that in use for so-called Berlin-wool work, the skins being held in position by means of strings, and dried by exposure in the open air. Parchment intended for drum skins (from calves' skins), for kettledrums (from asses' skins), does not require any further operation. If intended for bookbinding the parchment is treated as described, but after drying it is planed with a tool the cutting edge of which is somewhat bent in order to impart a rough surface, whereby the parchment is rendered capable of being written on and dyed. If the parchment be intended—as it used frequently to be formerly before the invention of metallic paper—for memoranda, written with lead-pencils, to be wiped out if desired with a wet sponge, it is after planing painted over with a thin white-lead paint, for which a mixture of glue-water with baryta- or zinc-white is often substituted. The vellum of this country is generally obtained from sheep skins, which are split into two sheets by means of cutting-tools. Parchment after having been dried on the frames is dusted over with chalk and rubbed with pumice-stone. The sieves used in powder mills for granulating the powder are made of parchment obtained from hogs' skins.

Shagreen. Genuine Oriental shagreen (saghir, sagri, sagre), is a variety of tawed parchment, one side of which is covered with small hard grains. This material is manufactured in Persia, at Astrakan, in Turkey, and in Roumania, from certain portions of the skins and hides of wild asses, horses, and other animals. The hides are soaked in water until the epidermis can be removed easily together with the hairs by the aid of a dressing-knife; next the hides are again placed in water so as to swell the material sufficiently to admit of cleansing it, and cutting away on both flesh and hair side all superfluous material, so as to leave only the corium, which then has the appearance of a fresh bladder. In order to produce on skins thus prepared a grained surface, they are put into frames, as described under Parchment, while on the hair side, *allabuta*, the hard black seed of the *Chenopodium album* is stamped in, either by the feet or forced in by pressure. When the skins are dry they are removed from the frame, the seed shaken off, and the skins thoroughly planed with a sharp dressing-knife, then put again into water, tawed, and finally dyed. The tawing is effected by the aid either of alum or of oak bark. The dye of shagreen is generally green, and is due to salts of copper. After dyeing the skins are soaked in mutton tallow.

Fish skin, or fish chagrin, is obtained from various kinds of sharks (*Squalus canicula*, *S. catulus*, *S. centrina*) and other fishes of the same class. The skin of these animals is not covered with scales, but with more or less projecting hard points. The skins having been removed from the fish are stretched in frames and simply dried, being then sent to the market. Formerly sharks' skin was in some countries used by joiners instead of sand- and glass-paper for preparing wood. The skins deprived of the projections are dyed and used for covering small boxes, tubes of small telescopes, &c.

GLUE-BOILING.

General Observations. The organisms of all animals, but more especially of the higher classes, contain tissues which are insoluble in cold as well as in hot water, but which by continued boiling become dissolved, and yield on evaporation of the solution a glutinous gelatinising mass, which, by further drying, exhibits, according to the degree of purity of the material, a more or less transparent and brittle substance, which in pure state is devoid of colour as well as of smell, becoming swollen in cold water and dissolved by boiling in that liquid. This substance, *i.e.*, the product of the conversion of the so-called glue- or gelatine-yielding tissues, is what is known in the trade as glue, and largely used by joiners, carpenters, &c., for joining wood, also for sizing paper, for clarifying various liquids, beer and wine for instance, and as a cement. Among the glue-yielding tissues the following are the most important:—Cellular tissue, the corium, tendons or sinews, the middle membrane of the vasa lymphatica and veins, the osseine or organic matter of bones, hartshorn, cartilage, the bladders of many kinds of fish, &c. Chemically we distinguish between glutin, that is to say, glue derived from skins, bones, &c., and chondrin, which has been obtained from cartilage. In a technical point of view this distinction is hardly required, as the cartilaginous matter is as much as possible selected from other glue-making materials, because experience has shown that glutin has a much greater power of adhesion than chondrin. The latter, however, is largely used as size in this country.

As already observed, the glue- or gelatine-yielding tissues yield on being dissolved a gelatinising mass, the aqueous solution of which does not, however, possess to any great extent a glueing property, which is only imparted to the gelatine by a process of drying. In considering, therefore, the process of glue-boiling, we have to distinguish the animal matter capable of yielding glue, the gelatinous mass obtained therefrom, and the glue obtained by drying the latter. The temperature required for obtaining gelatine differs according to the different animal tissues employed; the consistency of the gelatine obtained from equally strong solutions varies with the age of the tissues operated upon.

Glue readily dissolves by boiling in water, forming on cooling a gelatinous mass, even if the quantity of glue is only 1 per cent. Repeated boiling and cooling a glue solution causes it to lose the property of gelatinising, and the same effect is produced by acetic and dilute nitric acids. Solutions of alum precipitate glue solutions only after the addition of potash or soda, the precipitate consisting of glue mixed with basic sulphate of alumina. Glue enters with tannic acid into a combination of constant composition; hence glue or gelatine may be used for the estimation of tannin in vegetable matter.

Three different kinds of glue are distinguished by the manufacturers, viz.:—

a. So-called skin-glue, or leather-glue, prepared from refuse hides, skins, tendons, &c.
b. The glue obtained from bones.
c. The glue obtained from fish-bladders, termed isinglass.

Very recently glue from vegetable gluten and so-called albumen glue have been prepared.

Leather Glue. This substance is prepared from a large variety of animal refuse, the chief sources being the following:—Refuse from tan yards, tawing and leather-dressing works, old gloves, rabbit and hare skins (the hair having been used by hatmakers), skins of cats and dogs, ox feet, parchment cuttings, surons (skins which have served the purpose of carrying drugs, especially from America), sinews, guts, leather cuttings (leather tanned with oak bark cannot be readily converted into glue). The glue-boiler on an average obtains from the various materials about 25 per cent of glue, preference being given to the refuse of tawing operations and kid leather making, because these materials are ready for boiling without requiring any previous treatment. Glue-boiling involves the following operations:—

1. Treating the glue-yielding materials with lime.
2. Boiling these materials.
3. Forming the gelatine.
4. Drying the gelatine so as to form glue.

Treating with Lime. I. The aim of this operation is the cleansing of the refuse and the prevention of putrefaction. It is effected by placing the cuttings in tanks or lime-pits and pouring in a thin milk of lime. The materials, while the milk of lime is frequently renewed, are thoroughly mixed with the lime-liquid and left for fifteen to twenty days in the pits. By the action of the lime any blood and flesh is dissolved and the fatty matter saponified. In order to remove the excess of lime, the materials are placed either in nets or in willow-baskets, and these are immersed in a brook or river, where a continuous stream of fresh water removes the greater part of the lime in a few days. The washed material is next exposed in the yard to the action of the air in order that it may become dry, as well as form a carbonate of any lime still present in the materials. When the materials are dry they are packed and sent off to the glue-boilers, who, previous to proceeding with the boiling operation, macerate the materials again in a weak milk of lime, the maceration being followed by washing.

Fleck states that a weak alkaline ley (5 kilos. of calcined soda and 7·5 kilos. of quick-lime to 750 to 1000 kilos. of glue-yielding material) is preferable to the use of milk of lime. When the glue-boiling and tanning operations are executed on the same premises, the lime-treated glue materials are put for a few hours into old oak bark liquor, the acids (lactic, butyric, and propionic acids) of which remove the lime, while the animal matter is at the same time superficially tanned. This glue tannate rises during the boiling as scum to the surface and assists in rendering the glue liquor clear. According to Dullo, the Cologne glue—a very pale and strong glue—

is obtained from offal, which, after liming, has been treated with a solution of chloride of lime (hypochlorite of lime), and thereby bleached.

Boiling the Materials. This operation is carried on either in the ordinary manner of boiling anything with water, or by so-called fractioned boiling, or finally by the application of steam. As the conversion of the glue-yielding materials into glue takes place slowly and gradually under the influence of the boiling water, it is clear that the method of boiling cannot be without influence upon the glue ultimately produced. The first portions of gelatine which are formed remain in contact with a boiling-hot mass, and are thereby further changed so as to lose the capability of gelatinising, while the glue at last obtained exhibits a dark colour and is often not so strong, although it is generally believed that deep-coloured glue is of a better quality. A rational mode of glue-boiling would involve the gradual removal of the solution obtained, while of course fresh water would have to be supplied to replace the liquor drawn off. The older method of glue-boiling consists in simply placing the materials with water in a cauldron, care being taken to prevent burning by placing the materials on a stout wire gauze or tying them in a net and suspending it in the boiling liquid. Soft water yields a better result than hard. Gradually the materials become dissolved, and the scum which is formed is taken from the surface with a large ladle. The refuse of glue of former operations is added to the boiling liquid, and the operation continued until the liquid is of the required strength, which is tested by pouring into a broken egg-shell a small portion of the liquor, and by placing the partly-filled shell in ice-cold water. If the solution gelatinises after a while, forming a hard and rather stiff gelatine, the liquor is run off by means of a tap, filtered through a layer of straw placed in a basket, and conveyed to a wooden lead-lined cistern, externally covered with mats or straw, or some bad conductor of heat. In some works the liquor is decanted into a deep but narrow boiler, the furnace of which is so arranged as to impart heat to the top of the vessel only. This vessel, as well as the cistern, is heated previously to the liquor being poured in. The liquor is clarified by stirring it with a small quantity of very finely-pulverised alum, 0·75 to 1·5 per mille of the liquid. After this the liquid is left to stand all night. The alum precipitates any lime remaining as sulphate of lime, and also some organic matter which renders the liquid turbid. Alum, though it prevents the putrefaction of the glue while drying, impairs its strength. The lime might better be precipitated by oxalic acid, and the organic matter removed by adding to the boiling mass some astringent matter, such as oak bark decoction or hops, so that during the boiling the organic impurities could be taken away as scum.

Fractioned Boiling. By this operation only a comparatively small quantity of water is added to the animal matter intended to be converted into glue. When the water is fairly boiling the cauldron is covered with a well-fitting lid, and the steam being kept in as much as possible, is allowed to act upon the materials so as to convert them into glue. When, after continued boiling for about two hours, the water has taken up sufficient gelatine, the liquor is run off and fresh water poured on the materials. This operation is repeated until the decoction no longer gelatinises, the last liquor being kept for use instead of water for a following operation. The liquors thus obtained, excepting the last, are either mixed or each is treated separately. The glue yielded by the first decoction is stronger than that yielded by the subsequent liquors. By this method of boiling the saturated liquor does not remain exposed to the action of heat and water too long, and consequently a better article is produced. In some instances the materials intended to be converted into glue are boiled in a vessel similar in construction to those in use in bleaching-works and in paper-mills, arranged in the following manner. At some distance from the bottom a perforated false bottom is placed, in the centre of which is fixed a wide tube which reaches to about two-thirds of the height of the cauldron. The materials intended to be converted into glue are placed upon the perforated bottom and water under it; as soon as the water boils, the steam produced, not being able to escape rapidly and readily through the materials, exerts a pressure upon the liquid and forces it through the tube, the consequence being that a constant stream of boiling liquid falls upon the glue materials, which are rapidly dissolved.

A more rational mode of conducting this operation consists in employing high-pressure steam admitted into the mass of the animal materials to be converted into glue. In this manner a very concentrated solution of glue is obtained in a short time. In England steam is generally employed, but on the continent its use is the exception. It has been said that it is advantageous to allow the animal offal intended for glue to become somewhat decomposed and then to disinfect it with chlorine and sulphurous acid before boiling it for glue, because by this mode of treatment a brighter glue is obtained. We are unable to say whether this opinion is correct.

Moulding. As soon as the glue solution has, by standing in the tanks into which it had been transferred from the boilers, become quite clear and somewhat cooled, the liquid is poured into moulds, and when solidified the jelly is cut into cakes of the shape and size met with in the trade.

The moulds, into which the glue solution is poured through a strainer made of metal gauze, are of wood, and generally a little wider at the top than at the bottom, so as to admit of an easy removal of the solid material. At the bottom of the moulds a series of grooves are cut at such a distance from each other as agrees with the size of the intended glue-cakes. Before the liquid is poured into the moulds, these are thoroughly washed, and either allowed to remain damp, or if dried are oiled, so as to prevent the solidifying gelatine adhering to the wood. Recently moulds made of sheet-iron and zinc have been introduced. The moulds are filled with the lukewarm glue solution, and when the glue is sufficiently hard it is gently loosened from the sides with a sharp tool, and the mould having been turned over on a wooden or stone table, previously damped, is lifted off the block of gelatine, which is next cut into cakes or slabs. The cutting tool is simply a piano-wire, or more frequently a series of these stretched in a frame at sufficient distance from each other to make the cakes of the desired thickness, the frame being placed on small wheels so as to be easily moved. Glue is met with in the trade as a gelatinous mass, or is sold in casks under the name of size. It is said that the process of drying impairs the good qualities of the glue.

Drying the Glue. This operation is performed by placing the gelatine cakes on nets made of twine stretched in frames and exposed in a dry airy place to the action of the sun. The drying is one of the most difficult operations of the glue-making process, because the temperature of the air and its hygrometric condition exert a great influence on the product, especially during the first few days. The glue will not bear a temperature above 20°, because at a higher temperature it becomes again fluid, and as a matter of course flows through the meshes of the net and adheres to the twine so strongly as to require the nets to be put into hot water for the removal of the mass. Too dry air causes an irregularity in the drying of the glue, and as a consequence the cakes become bent and cracked; while frost causes disintegration, so as to necessitate a re-melting of the glue; hence it follows that drying in the open air can only be effected in the spring and autumn. Although the glue-boilers have tried to dry glue by artificial heat, this plan has not been generally introduced owing to the fact that a slight excess of heat causes the melting of the gelatine, the more readily when ventilation is neglected. Drying-rooms, as recently constructed are large-sized sheds fitted with the required frame-work for receiving the gelatine cakes, and heated by steam-pipes placed on the floor near the latter. The walls are provided with openings which can be closed by means of valves, while there are ventilators in the roof arranged to obtain a proper circulation of air. As the gelatine placed nearest to the floor of the room becomes most quickly dry, it is, with the frames upon which it placed, removed after eighteen to twenty-four hours to a higher part of the drying-room, which is not heated at all if the outer air has a temperature of 15° to 20°. The drying-shed, or room, is by preference built so as to face the north. When the glue has been thus dried as much as possible, it is generally quickly dried in a stove in order to impart hardness. It is next polished by being immersed in hot water, and cleaned with a brush, and again dried.

Glue from Bones. The organic matter contained in bones, forming nearly one-third part (32·17 per cent) of their weight, consists of a material which, after the bones have been treated with hydrochloric acid, is very readily converted by the action of high-pressure steam into glue. The preparation of glue from bones by the action of hydrochloric acid is the usual mode of proceeding, and the operation is advantageously combined with the making of sal-ammoniac and phosphorus.

The preparation of glue from bones includes the following operations:—I. *Boiling out the Grease.*—The bones are put into water and boiled in a cauldron, the fat floating to the surface. Frequently in order to save fuel the bones are put into an iron wire basket, which is removed after the boiling has been continued for some time, the bones thrown out and fresh ones put in, the boiling being continued until a thick gelatinous liquor is obtained. The fat or grease is removed from the surface of the liquid by means of ladles. The gelatinous mass obtained by this process is either used as a manure or is given to cattle as fodder. In some works bones have been exhausted with sulphide of carbon for the purpose of extracting the grease. II. *Treating the Bones with Hydrochloric Acid.*—The bones having been drained are placed in baskets, and with these are immersed in tanks to more than half their height, the tanks being filled with hydrochloric acid at 7° B. (= 1·05 sp. gr. = 10·6 per cent ClH); 10 kilos. of bones require 40 litres af acid. The bones are kept in this liquor until they become quite soft and transparent. They are next drained and then with the baskets immersed in a stream or brook with a good supply of running water to wash out the greater portion of the acid, which is fully neutralised by placing the bones in lime-water, again followed by washing with fresh water, the bones being then ready for boiling. Gerland has suggested the use of sulphurous instead of hydrochloric acid. III. *Conversion of the Organic Matter into Glue.*—The cartilaginous substance having been either partly or completely dried is put into a cylindrical vessel containing a false perforated bottom, and between that and the real bottom a pipe or tube. To the top of the vessel a lid is fitted, provided with an opening for a steam-pipe leading from a small boiler. Shortly after the admission of the steam a concentrated glue solution begins to run off from the pipe at the bottom of the cylinder; this solution is usually so concentrated as to admit of being at once run into the moulds, and after having become solid is treated as before described. After a few hours a weak liquid makes its appearance, and as soon as this happens the cylindrical vessel is opened, the glue mass removed with the weak liquid to a copper and boiled, care being taken to stir the magma constantly. As soon as the glue is dissolved the liquor is poured into moulds. Glue obtained from bones exhibits a milky appearance due to the presence of a small quantity of phosphate of lime retained in the substance. Sometimes there is purposely added more or less baryta-white, zinc-white, white-lead, chalk, or pipe-clay. The glue obtained from bones is sold under the name of patent glue.

Liquid Glue. When glue is dissolved in its own weight of water and a small quantity of nitric acid added to the solution, it loses the property of gelatinising, while the adhesive property of the glue is not impaired. Dumoulin prefers to dissolve 1 kilo. of Cologne glue in 1 litre of boiling water, and to add to the solution 0·2 kilo. of nitric acid at 36 B. = 1·31 sp. gr. After the evolution of the nitrous acid fumes has subsided the fluid is cooled. A better liquid glue is obtained by dissolving good gelatine or glue of superior quality in strong vinegar and moderately strong acetic acid, to which one-fourth of its bulk of alcohol is added, and some pulverised alum, the solution being aided by a water-bath. The action of the acetic acid is the same as that of the nitric acid. According to Knaffl, a very excellent liquid glue is obtained by heating for some 10 to 12 hours upon a water-bath, a mixture of 3 parts of glue in 8 parts of water, to which are added 0·5 part of hydrochloric acid, and 0·75 part of sulphate of zinc, the temperature of the mixture being kept below 80° to 85°. This kind of liquid glue keeps for a very long time and is largely used for joining wood, horn, and mother-of-pearl. This glue is employed by the makers of artificial pearls.

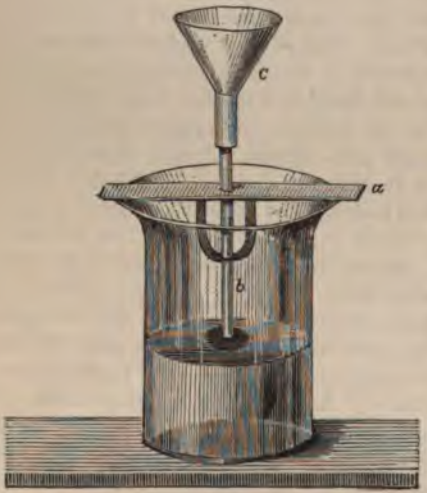
Test for the Quality of Glue. Although the quality of glue is best ascertained by practical use, some of the physical qualities and the external appearance of glue may be mentioned as indicating a superior article. Glue of good quality should exhibit a bright brown or brown-yellow colour, should be free from specks, glossy, perfectly clear, brittle, and hard, should not become damp by exposure to air; when being bent it should snap or break sharply, the fracture presenting a glassy, shining appearance. When placed in cold water glue should not even after forty-eight hours in this fluid swell up and increase in bulk nor dissolve. A splintery fracture of glue indicates that it has not been well boiled. The adhesive property of glue is often increased by adding certain pulverulent earthy substances. This addition is regularly the case with Russian glue. Among the substances employed are white-lead, sulphate of lead, zinc-white, baryta-white, and even chromate of lead. As different kinds of glue may agree in their external aspect and yet vary as regards their adhesive power, methods of testing glue have been proposed, some of which are based upon the chemical, others upon the physical, properties of this substance.

I. *Chemical Processes of Testing Glue.*—Of these we mention the following:—Graeger's Method.—Premising that the quality of a glue is dependent on the quantity of glutin contained, irrespective of the origin of the glue and its freedom from foreign substances, which might weaken its adhesive property, Graeger estimates the quantity of gluten by precipitating the glue solution with tannin, and by calculating from the amount of tannate of gelatine obtained (the composition being taken in 100 parts at 42·74 parts of gluten and 57·26 of tannin), the quantity of pure gluten contained in the glue. Risler-Beunat, while employing the same principle, prepares two normal fluids, one of which contains 10 grms. of pure tannic acid to the litre, while the other contains in 1 litre 10 grms. of pure isinglass and 20 grms. of alum. As equal bulk of these fluids do not saturate each other, the author determines by titration the relation between them, and dilutes the tannic acid solution with the requisite quantity of water. In order to test a glue the author dissolves 10 grms. of the sample to be tested with 20 grms. of alum in a litre of water, heat being applied if necessary. Next 10 c.c. of the tannic acid solution are taken, to which an equal bulk (10 c.c.) of the glue solution is at once added, because one may be sure that this is not too much, as no sample of glue met with in commerce is as pure as isinglass. The vessel containing the mixed liquid being well shaken and the precipitate having settled, another c.c. of glue solution is added to the tannin solution, which is next filtered through a moistened cotton filter. If *one* drop of the glue solution still produces a precipitate in the clear filtrate another c.c. is added to the tannin solution, and then again filtered, these operations being repeated until the filtrate is no longer rendered turbid by the glue solution.

These modes of testing glue give only an approximate value of the glue, as its precise chemical constitution is not known, and is, in all probability, complex; while it has not been proved that the substance combined with tannin corresponds to the adhesive power of glue. Finally, it should be observed, that gelatine and glue, though both precipitated by the same quantity of tannin, are altogether different substances.

II. *Mechanical Modes of Testing Glue.*—Schattenmann's Method.—The glue to be tested is kept immersed for a considerable time in a large quantity of water at 15°; the substance swells up, absorbing five to sixteen times its own weight of water. The more consistent and elastic glue is found to be in this state the greater its adhesive power. The larger the quantity of water absorbed the more economical will the glue be in use. According to Weidenbusch's experiments, this method should be employed only with glue obtained from bones, as that obtained from animal offal does not behave similarly. Lipowitz has proposed the following method:—5 parts of glue are dissolved in such a quantity of water that the weight of the solution is equal to 50 parts. This solution is kept for twelve hours at 18° in order to cause the solution to gelatinise. The gelatine obtained is placed in a glass vessel, Fig. 256. *a* is a piece of tinned iron through which the iron wire *b* moves easily. At the lower end of *b* is soldered a saucer-like piece of tinned iron, the convex side of which is turned downwards. The weight of the wire *b* and the convex piece soldered to it is 5 grms., while the funnel, *c*, put on the top of the wire

Fig. 256.



also weighs 5 grms. The funnel is of sufficient size to contain 50 grms. of small shot. According to the consistency the greater weight will it require to force the gelatine down into the glass, and from the weight required the adhesiveness may be judged. Heinze has tried this method (1864), and the results of his experiments prove the correctness of Lipowitz's proposition.

Weidenbusch's method is essentially that suggested by Karmarsch, and consists in testing the weight required to tear asunder two pieces of wood glued together with the sample of glue; but it is evident that this plan is not satisfactory, because it is impossible to obtain wood always of the same quality, while the adhesiveness of good glue is greater than that of wood itself. Weidenbusch has evidently observed that the method is not reliable, for he has suggested the following plan:—Small sticks or rods are made of gypsum, are gently dried, first by heat and next over chloride of calcium until the rods do not lose weight. They are then saturated with solutions of samples of glue; the force required to break these rods after drying determines the strength of the glue, because the force required to break the gypsum is of a constant value. An apparatus has been contrived by the aid of which the weight required to tear asunder the dried gypsum rods may be ascertained; the average weight has been found to be 219 grms. The glue to be tested is dried at 100°, put over night into cold water, next dissolved in hot water, the solution being so arranged as to contain one-tenth of glue. This solution is coloured with neutral indigo tincture in order to render it more easily discernible. The gypsum rods are left in the solution for a couple of minutes and then dried until the weight does not vary. When this obtains the rods are broken by the action of mercury, which is gradually admitted into the apparatus.

Isinglass. The substance met in commerce under the name of isinglass is, if genuine, the dried interior pulpous vesicular membrane of the air-bladder of certain kinds of fish belonging to the order of the cartilaginous ganoids, and more especially of the common sturgeon (*Accipenser sturio*); the huso, or grand sturgeon (*A. sturio*); the *A. Güldenstaedti*, and *A. stellatus*. The bladders of these and of kindred species of fish plentifully met with in the Caspian Sea and the estuaries of the rivers running into it, are cut open, cleansed, stretched, and dried by exposure to sunlight, and when sufficiently dry to admit of being handled without fear of tearing the outer muscular membrane, which does not on being boiled yield any glue, is torn off, while the interior membrane is moulded in various ways (as in rings, lyre-shaped, or folded as leaves of paper), and bleached by sulphurous acid, then thoroughly dried by exposure to sunlight.

According to the countries from which it is sent into the trade isinglass is distinguished,—as Russian (the best kind being obtained from Astrakan); North American (from *Gadus merlucius*); East Indian (from *Polynemus plebejus*), met with in leaves, also as small sacks, and in the entire bladder; Hudson Bay isinglass (derived from sturgeons); Brazilian is probably obtained from various kinds of *Silurus* and *Pimeladus*. This isinglass occurs in hollow tubes, in lumps, and in discs. German isinglass is prepared at Hamburg from the air-bladder of the common sturgeon. In Roumania and Servia the skin and intestines (not the liver) of cartilaginous fishes are boiled into a stiff jelly, which, having been cut into thin slices, is dried and sent into the market as isinglass. As regards the use of this material we have to distinguish between fish glue and isinglass. The former, if properly prepared, is not at all distinguishable from ordinary glue as obtained from bones or other animal refuse; but isinglass is not glue, and is only converted into it by boiling. It consists of fibres or threads, which when placed in water are somewhat dissolved, but retain their organised structure; this being especially of importance for the use of this substance in clarifying wine, beer, and similar fluids, as the fibres constitute as it were a close network, which readily takes up the turbidity produced by small particles. The presence of tannin in liquids which are intended to be clarified by the use of isinglass is advantageous, inasmuch as it promotes the contraction of the isinglass fibres, whereby the suspended particles present in the fluid to be clarified are retained; so that in truth the clarifying by isinglass is a kind of filtration, which cannot be performed either by glue or by a hot saturated solution of isinglass. For isinglass may, in all other instances, such as the dressing of woven silk fabrics, the preparation of so-called court-plaster and cements, be substituted good gelatine. Under the name of *Ichtyocolle Française*, Rohart some years ago introduced a substitute for isinglass, a compound said to be obtained from fibrin of blood and tannin.

Substitutes for Glue, and New Preparations obtained from Glue.

Recently three substitutes for glue have been introduced, viz.:—1. Gluten glue (*colle gluten*). 2. Albumen glue (*colle végétale ou albuminoide*. 3. Caseine glue (*colle caseine*). The first is a mixture of gluten and fermented flour. It is a very sour mixture, endowed with but very slight adhesive power. Albumen glue is partially decayed gluten, the substance largely obtained in the manufacture of starch from wheaten flour thoroughly washed with water, and then exposed to a temperature of 15° to 20°, at which it begins to ferment and become partly fluid, or more correctly soft, so as to admit of being poured into moulds which are placed in a room heated to 25° or 30° for twenty-four to forty-eight hours. The surface having become dry enough to admit of the cakes being handled, they are taken from the moulds and further dried by being placed either on canvas or on wire gauze. After four to five days the cakes are quite dry and fit for being kept in a dry place for any length of time. A solution of this substance in twice its weight of water constitutes a normal solution, which may be diluted according to the use desired to be made of it. This kind of glue may be used for the following purposes:—Glueing wood, cementing glass, porcelain, earthenware, mother-of-pearl, for pasting leather, paper, and cardboard; it may further serve as weaver's glue, and as dressing for silk and other woven fabrics; also for a mordant instead of albumen in dyeing and printing various fabrics; and lastly, for clarifying liquids.

Caseine glue is prepared by dissolving caseine in a strong solution of borax. The thick fluid thus obtained has great adhesive powers and may be advantageously employed by joiners and bookbinders. What is known as elastic glue is a preparation of glue and glycerine, by the addition of which glue may be rendered permanently elastic and soft. It is prepared in the following manner:—Glue is melted in water by the aid of a water-bath, into a very thick paste, to which glycerine is added in the same quantity by weight as that of the dry glue. The mixture is thoroughly stirred and then further heated in order to evaporate the excess of water. The mass is then cast on a marble slab, and after cooling, serves for the purpose of making printer's inking rollers, elastic figures, galvano-plastic moulds, &c.

MANUFACTURE OF PHOSPHORUS

General Properties. Phosphorus was discovered in 1669 by Brand, at Hamburg, and prepared by him from urine. In 1769, Gahn, a Swedish chemist, first prepared this element from bones; his mode of preparation being improved in 1771 by his celebrated countryman, Scheele. Since the introduction of phosphorus matches, its manufacture has become one of the most important technical operations. Phosphorus occurs largely in the mineral kingdom as phosphoric acid, but for the manufacture of phosphorus in sufficient quantity only in such minerals as apatite, phosphorite, and staffelite.

Phosphorite is found in various localities, as, for instance, near Diez, Weilburg, and Amberg and Redwitz in Bavaria. Some of this phosphorite is very rich in phosphoric acid, a sample of that found near Diez having yielded on analysis (by Petersen, 1866), 37·78 per cent of phosphoric acid, corresponding to 16·06 per cent of phosphorus.

Preparation of Phosphorus. Bone-ash is now the only material used by phosphorus makers, as the commercial preparation of phosphorus has not succeeded by using either apatite and other varieties of pure phosphorite which contain about 18·6 per cent of phosphorus—as well as sombrerite (a mineral met with on the American island of Sombrero), consisting of phosphate and carbonate of lime, and imported into England for the manufacture of superphosphates; or the Navassa guano, also imported from the United States, containing, according to Ulex's researches, one-third of its weight of phosphoric acid; or phosphate of iron, as proposed by Minary and Soudray, by distilling that substance with previously well-ignited coke-powder.

Bones, as used by the manufacturers, contain :—

In dry state, but not ignited, from 11 to 12·0 per cent of phosphorus.
As bone-black „ 16 to 18·0 „ „ „ „
As bone-ash (white burnt bones) „ 20 to 25·5 „ „ „ „

The composition of bone-ash is exhibited by the following results of analysis :—

	1.	2.
Carbonate of lime	10·07	9·42
Phosphate of magnesia	2·98	2·15
Tribasic phosphate of lime	83·07	84·39
Fluoride of calcium...	3·88	4·05

The bone-ash is decomposed by means of sulphuric acid, according to a plan first suggested by Nicolas and Pelletier :—

$$a.\ \left.\begin{matrix}\text{Bone-ash, } Ca_3(PO_4)_2\\ \text{Sulphuric acid, } 2H_2SO_4\end{matrix}\right\}\text{yield}\left\{\begin{matrix}\text{Acid phosphate of lime, } CaH_4(PO_4)_2\\ \text{Sulphate of lime, } 2CaSO_4.\end{matrix}\right.$$

The acid phosphate of lime is heated with charcoal, and converted by loss of water into metaphosphate of lime :—

$$b.\ \underbrace{\left.\begin{matrix}Ca\\ H_4\end{matrix}\right\}(PO_4)_2}_{\text{Acid phosphate of lime.}}-2H_2O=\underbrace{Ca(PO_3)_2}_{\text{Metaphosphate of lime.}}$$

The metaphosphate of lime yields, when ignited to white-heat with charcoal, two-thirds of its weight of phosphorus, while one-third remains in the residue:

$$c.\ \left.\begin{array}{l}\text{Metaphosphate of lime, } 3Ca(PO_3)_2\\ \text{Charcoal, } 10C\end{array}\right\}\text{yield}\left\{\begin{array}{l}\text{Tribasic phosphate of lime, } Ca_3(PO_4)_2\\ \text{Carbonic oxide, } 10CO\\ \text{Phosphorus, } 4P.\end{array}\right.$$

The ordinary mode of preparing phosphorus includes the following operations:—

In some instances the preparation of phosphorus is cotemporary with other businesses, viz., glue-boiling, the preparation of sal-ammoniac, yellow prussiate of potash, &c., but generally in England the phosphorus makers do not even burn the bones to ashes, but purchase bone-ash and occasionally apatite; this salt, however, is very difficult to treat with sulphuric acid, and is also objected to on account of its hardness, for it has to be ground to a very fine powder. English makers only carry out these four:—

1. Burning the bones and grinding the bone-ash to powder.
2. Decomposition of the bone-ash by sulphuric acid, and evaporation of the acid phosphate previously mixed with charcoal.
3. The distillation of the phosphorus.
4. The refining and preservation of the phosphorus.

Burning of the Bones to Ash. 1. The bones to be used for phosphorus making are obtained either from bone-boilers or from the waste bone-black of sugar-refiners. The aim of the ignition of the bones is the complete destruction of the organic matter. The operation is conducted in a kiln very similar to those in use for burning lime. A layer of brushwood having been put at the bottom of the kiln, bones form the next stratum, and so on alternately. The wood having been lighted, the combustion of the bones ensues. In order to carry off the fumes, the smell of which is very offensive, a hood made of boiler-plate is placed on the kiln, and either connected with a tall chimney, or the smoke and gases are conducted into the fire of the kiln and burnt. The white burnt bones are withdrawn through an opening reserved in the wall on purpose, the kiln being kept continuously in operation, as is the case with some lime-kilns.

100 kilos. of fresh bones yield from 50 to 55 kilos. of white burnt bone-ash, which is converted into a coarse powder by means of machinery.

Decomposition of the Bone-Ash by Sulphuric Acid. 2. 100 kilos. of the bone-ash, of which about 80 per cent is tribasic phosphate, require for decomposition:—

106·73 kilos. sulphuric acid of 1·52 sp. gr.
85·68 „ „ „ „ 1·70 „ „
73·63 „ „ „ „ 1·80 „ „

Payen advises that for 100 kilos. of bone-ash 100 parts of sulphuric acid at 50 per cent or 1·52 sp. gr. be taken. The operation of mixing the acid and bone-ash is effected in lead-lined wooden tanks, or in wooden tubs internally coated with pitch or coal-tar asphalte. The liquor decanted from the precipitate has a sp. gr. of 1·05 to 1·07 = 8° to 10° B. The sediment is lixiviated with water, and the liquor obtained (= 5° to 6° B.) evaporated with the first liquor in leaden pans. A second lixiviation of the sediment yields a fluid which is used instead of water for the purpose of diluting the oil of vitriol. The evaporation in the leaden pans (these are smaller, but otherwise similar in construction to those used for evaporating sulphuric acid) is continued until the fluid has attained a sp. gr. of 1·45 = 45° B., when it is mixed with charcoal-powder, or rather granulated charcoal, of the size of small peas, in the proportion of 20 to 25 parts of charcoal to 100 of liquor, and quickly dried after having been put into cast-iron pots placed on a furnace.

The dry mass consists of phosphate of lime, carbon, and water, to an amount of 5 to 6 per cent. At the commencement of the manufacture of phosphorus the idea prevailed that in the preceding preparation the phosphoric acid was present in free state, while the lime had combined with sulphuric acid; but Fourcroy and Vauquelin finding that the tri-basic phosphate of lime as met with in bone-ash ($Ca_3(PO_4)_2$) was, by the action of the sulphuric acid, converted into acid phosphate of lime ($CaH_4(PO_4)_2$), supposed that more sulphuric acid was required, an opinion opposed by Javal, who proved that when pure phosphoric acid is intimately mixed with carbon, it yields only a small quantity of phosphorus, because the acid is volatilised at a temperature lower than that required for its decomposition, or rather reduction by carbon. Owing to the presence of water in the mixture, there is given off during the distillation in addition to oxide of carbon, carburetted and phosphuretted hydrogen.

Distillation of Phosphorus. 3. The mixture of acid phosphate of lime and charcoal is distilled in fire-clay retorts similar in shape to those used for distilling Nordhausen sulphuric acid, while the furnace in which these retorts are placed is also similar in construction and holds twelve retorts on each side. The body of the retorts is placed on the side of the fire, while the neck passes through an opening in the wall of the furnace, that portion of the wall being only lightly bricked up, as the retorts, after the distillation is finished and the furnace cooled, have to be removed, in order to clear out the residue and introduce fresh mixture. Between each pair of retorts is left a space of some 12 to 15 centims., in order to afford room for the passage of the flame. As already mentioned, the heat causes the acid phosphate of lime ($CaH_4(PO_4)_2$), to be converted into metaphosphate of calcium ($Ca(PO_3)_2$), which, with increased heat, gives off two-thirds of its phosphorus, there being left in the retorts one-third in the shape of tri-phosphate of calcium ($Ca_3(PO_4)_2$). The receivers used in Germany are constructed in the following manner:—The material is clay, glazed. The receiver consists of two parts, one of which is a cylindrical vessel open at the top, into which the other part fits, and is fixed by means of a rim which is prolonged so as to form a neck, between which and the first part is inserted a tube fitted on the neck of the retort, while the other end of this tube dips for about 10 centims. into the receiver, the latter being filled with water. Into each retort 6 to 9 kilos. of the mixture intended to be operated upon are introduced; the retorts are then placed in the furnace and the brickwork is restored. This having been done, the fire is kindled and kept up very gently for some time in order to dry the fire-clay used in joining the bricks. The receivers are filled with water and fitted to the retorts. In each receiver a small iron spoon is placed fastened to an iron wire which serves as a stem. After six to eight hours' firing the heat has been so much increased as to cause the expulsion of any moisture left in the material placed in the retorts, while quantities of hydrocarbon gases and oxide of carbon are formed and with sulphurous acid expelled. Subsequently other gases are given off, and because they contain some phosphuretted hydrogen are spontaneously inflammable. As soon as this phenomenon is observed, the joints of the receivers and apparatus connecting it with the retort are luted with clay, care being taken to leave by the insertion of an iron wire a small opening for the escape of the gases, which are as speedily as possible removed by well-arranged ventilators from the building in which the furnace is placed. The appearance of amorphous phosphorus at the small opening indicates the commencement of the distillation. The spoon is then placed in the receiver in such a direction that any phosphorus coming over may collect in it. During the progress of the operation, and as long as any phosphorus distils over, the evolution of combustible gases continues, and consequently a small blue-coloured flame is observed at the opening in the lute. The water in the receivers is kept cool during the operation. After forty-six hours, with a greatly increased firing, a full white-heat is reached, and the quantity of phosphorus coming over has decreased so much as to make a continuation of the ignition process wasteful. The receivers are therefore disconnected from the retorts, and the crude phosphorus, a mixture of silicide of phosphorus, carburet of phosphorus, amorphous phosphorus, and other allotropic modifications of this element, is poured into a tub containing water. The furnace having become cool is broken up and the retorts are removed, the contents taken out with an iron spatula, and the retorts replaced after having been re-filled with fresh mixture. 100 kilos. of the mixture yield about 14·5 kilos. of crude and 12·6 kilos. of refined phosphorus. As to Wöhler's method of preparing phosphorus by the ignition of a mixture of charcoal, sand, and bone-ash, the process is not well adapted for practical use, because it requires a very high temperature, which would melt, or nearly so, and at any rate soften, the retorts. Moreover, the proposed mixture contains only one-third the quantity of phosphoric acid met with in the mixture now in general use.

Fig. 257.

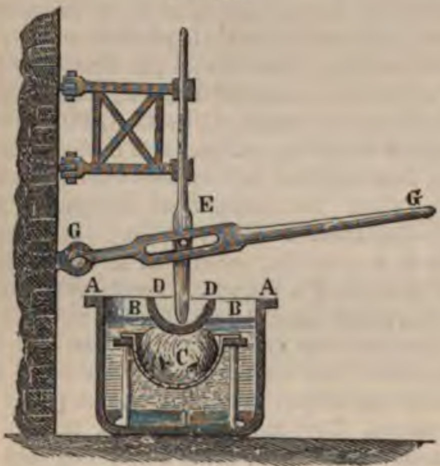


Fig. 258.

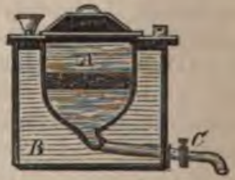
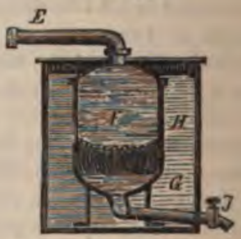


Fig. 259.



Refining and Purifying the Phosphorus.

4. As already stated, the crude phosphorus is contaminated with carbon, silicium, red and black phosphorus, and various other impurities, which in former days were eliminated by forcing the phosphorus through the pores of stout wash-leather by means of a machine exhibited in Fig. 257, C representing a tightly-tied piece of wash-leather containing the crude phosphorus, the bag being placed on a perforated copper support, situated in a vessel filled with water at 50° to 60°. As soon as the phosphorus is molten, there is placed on the wash-leather a wooden

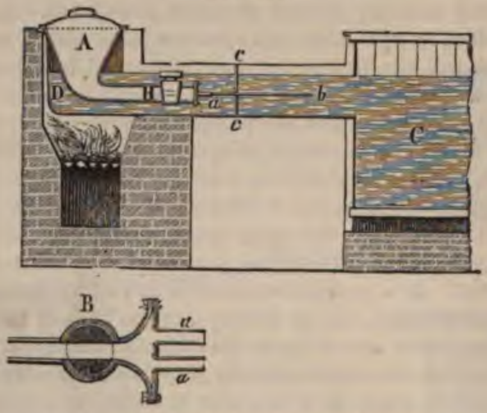
plate, D D, which by the aid of the mechanical arrangement K, and the lever, G G, can be forced downwards so as to cause the fluid phosphorus to pass through the pores of the leather, the impurities being retained. More recently French manufacturers have introduced another system of purifying phosphorus, viz.:—*a*. By filtration through coarsely-powdered charcoal, which is placed in a layer of 6 to 10 centims. on a perforated plate of the vessel A, Fig. 258, two-thirds filled with water, kept by means of the water-bath, B, at a temperature of 60°. The molten phosphorus placed on A passes through the layer of charcoal, and is thereby purified. It flows through the open tap C and the tube E, being collected in the vessel F filled with water, maintained by means of the water-bath, G, at a temperature sufficiently high to render the phosphorus fluid, so that it may, when aided by hydraulic pressure, pass through the perforated bottom, H, and the wash-leather spread over it. The filtered phosphorus may be run off by means of the tap J.

According to another process of purification (*b*), porous, unglazed porcelain or earthenware plates are fixed in an iron cylinder connected with a steam-boiler. The steam yielded by the latter forces the molten phosphorus—previously mixed with charcoal powder for the purpose of preventing the pores of the plates becoming choked—through the earthenware plates. The charcoal containing some phosphorus is used in the distillation of the phosphorus. This method of purification yields from 100 kilos. of crude, 95 kilos. of refined, phosphorus. In Germany crude phosphorus is purified by distillation, this operation being carried on in iron retorts of a peculiar make and shaped like the glass retorts used in chemical laboratories. The neck of these retorts dips for a depth of 15 to 20 millimetres in water contained in a basin filled to the rim, so that any phosphorus which is discharged into this water causes it to overflow. The crude phosphorus having been fused under water is next mixed with 12 to 15 per cent of its weight of moist sand, and this mixture is placed in the retorts in quantities of 5 to 6 kilos., the object of the mixing with sand being to prevent the phosphorus becoming ignited during the filling of the retorts. Crude anhydrous phosphorus yields by this process of distillation about 90 per cent of the refined product. In a phosphorus manufactory at Paris the crude phosphorus is purified by chemical means, viz., by mixing with 100 kilos. of the crude substance 3·5 kilos. of sulphuric acid and the same quantity of bichromate of potash; a slight effervescence ensues, but the result is that the phosphorus is rendered very pure, and may, after washing with water, be at once cast in the shape of sticks. The yield of refined phosphorus by this process is 96 per cent.

Moulding the Refined Phosphorus. It has long been the custom to mould phosphorus into the shape of sticks formed by the aid of a glass tube open at both ends, one of these being placed in molten phosphorus covered by a stratum of warm water. The liquid phosphorus is sucked by the operator into the tube until it is quite filled. The lower opening of the tube being kept under water is closed by the finger of the operator; the tube is instantly transferred to a vessel filled with very cold water, by which the phosphorus is solidified. It is removed from the glass tube by pushing it out with a glass rod or iron wire while being held under water. Instead of suction by the mouth, a caoutchouc bag similar to that used in volumetric analysis for the purpose of sucking liquids into pipettes may be employed. In the French phosphorus works the glass tubes are fitted at the top with an iron suction tube provided with a stop-cock. The operator, who has from one to two thousand of these tubes at his disposal, sucks, either by mouth or with a caoutchouc bag, the molten phosphorus into the glass tube, and having turned off the stop-cock, rapidly transfers the tube to a vessel filled with cold water. When all the tubes are filled the phosphorus is removed by opening the stop-cock and pushing the stick out by the aid of a wire. A clever workman may mould in this way 2 cwts. of phosphorus daily.

Another mode of performing the moulding has been introduced by Seubert. The apparatus contrived by him for this purpose is exhibited in Fig. 260, and consists of a copper boiler fitted on a furnace; to the flat bottom of this boiler is fastened by hard solder an open copper trough communicating with the water-tank, C. In the boiler is fitted a copper funnel, A, provided with a horizontal tube, B. This portion of the apparatus is intended for the reception of the phosphorus, of which it will hold 8 to 10 kilos. At the end of the horizontal tube, B, is placed a stop-cock, H, while the portion of the projecting mouth of the tube beyond the cock is widened out and fitted by means of bolts and nuts with a flange-like copper plate, into which are inserted two glass tubes, *a a*. Into the copper trough is let a wooden partition, *c c*, which serves the purpose as well of supporting the glass tubes as of preventing the communication of the hot water in the boiler and a portion of the trough with the cold water of the tank and the portion of trough nearest to it. The vessel A having been filled with refined phosphorus, the water in D is gently warmed so as to cause the fusion of the phosphorus. As the warm water reaches to the partition, *c c*, it is clear that on opening and closing the tap B, some phosphorus will pass through and flow out of the tubes *a a*, but that remaining in these tubes will solidify, and on opening the tap B again the solid sticks of phosphorus may be removed from the glass tubes by taking hold of the piece of projecting phosphorus the phosphorus being immediately immersed under water in the tank C, and kept there protected from the action of the light. While, according to Seubert, it would be possible for a workman to mould in an hour's time 30 to 40 kilos. of phosphorus, Fleck has found, that under the most favourable conditions of temperature, it takes six hours to mould 50 kilos. of phosphorus. If it is desired to prepare granulated phosphorus with this apparatus, a stratum of 6 to 8 centims. thickness of hot water is so carefully poured on cold water as not to mix; next the tap B is opened sufficiently to cause the phosphorus to form drops, which, immediately on falling into the cold

FIG. 260.



water, becomes a hard solid mass. For practical purposes granulated phosphorus is preferable to the moulded sticks. The phosphorus is stored either in strong sheet-iron tanks or in wooden boxes lined with thinner (tinned) sheet-iron, these vessels being capable of holding 6 cwts. of phosphorus covered with a stratum of water fully 3 centims. deep. When large quantities, say, from 1 to 5 cwts., of phosphorus have to be sent off, it is usually packed in water in small wine casks, and the casks having been tightly closed, are coated externally with molten pitch, then rolled through chaff, and lastly covered with stout canvas sewed tightly round the cask. Another method of packing phosphorus consists in placing it in well-made water-tight sheet-iron or tinned iron canisters, such as are largely used in London for the purpose more particularly of conveying oil paints, and which are closed by soldering on a lid very securely. In some cases these canisters are packed in wooden boxes to the number of six or twelve according to size and weight.

Other Proposed Methods of Preparing Phosphorus. Among the many suggestions as to the preparation of phosphorus, we may mention Donovan's plan of obtaining this element by the calcination of a mixture of finely divided charcoal and phosphate of lead, prepared by digesting 10 kilos. of broken-up bones with 6 kilos. of nitric acid, and 40 litres of water; this liquid, after having been decanted from the gelatinous material of the bones, is treated with a solution of 8 kilos. of acetate of lead. The washed and dried precipitate of phosphate of lead is next ignited, and afterwards, when cold, mixed with one-sixth of its weight of lamp-black or charcoal powder. Cari-Montrand exposes a mixture of bone-ash and carbonaceous matter at red heat to the action of hydrochloric acid gas:—

$$\left.\begin{array}{l}\text{Calcium tri-phosphate, } Ca_3(PO_4)_2\\ \text{Carbon, } 8C\\ \text{Hydrochloric acid, } 6ClH\end{array}\right\}\text{yield}\left\{\begin{array}{l}\text{Phosphorus, } P_2\\ \text{Chloride of calcium, } 3CaCl\\ \text{Hydrogen, } 3H_2\\ \text{Carbonic oxide gas, } 8CO\end{array}\right.$$

Neither of these methods have been tried practically on the large scale.

Fleck's Process. By this method the preparation of phosphorus is allied to that of glue- and size-making. The process is based upon the solubility of phosphate of lime in hydrochloric acid, and the separation of an acid phosphate of lime on the evaporation of the solution, carried on in earthenware evaporating basins. Theoretically, 156 parts of tribasic phosphate of lime ($Ca_3(PO_4)_2$) require 73 parts of anhydrous hydrochloric acid, whereby are formed—of chloride of calcium, 111; of acid phosphate, 100; and of water, 18 parts. By the ignition of 100 parts of acid phosphate of lime with 20 parts of carbon, are generated—of phosphorus, 21·3; of tri-phosphate of lime, 52; and of oxide of carbon, 46·7 parts.

By re-heating the tri-phosphate of lime remaining in the retorts with hydrochloric acid another portion of acid phosphate of lime might be obtained; and as far as experiments have been made, it is proved that it is possible to extract all the phosphorus contained in bones, by working with hydrochloric acid free from sulphuric acid, and carefully evaporating the acid solution thus obtained. Practically the process includes the following operations:—1. Cleaning, breaking up, and exhausting the bones. 2. The evaporation of the acid liquid; crystallisation of the acid phosphate, and mixing of the latter with charcoal. 3. The distillation and purification of the phosphorus; and finally,—4. The glue boiling. The bones, previously crushed and deprived by boiling of the fat they contain, are macerated in dilute hydrochloric acid at 7° B.=sp. gr. 1·048, and then in a stronger acid at 30° B.=sp. gr. 1·246, in which the bones are left until they have become quite soft. The liquid which has served this purpose is afterwards employed with water in preparing the first acid liquor for the exhausting of the bones. The first liquor, a solution of acid phosphate of lime (superphosphate) and chloride of calcium, obtains a sp. gr. of 1·118 = 16° B. This acid liquid is evaporated, but this operation cannot be proceeded with in leaden vessels, and there is some difficulty in finding very large evaporating basins made of porcelain or earthenware which will answer the purpose. As soon as the liquor has reached a density of 30° B = sp. gr. 1·246, it is sufficiently concentrated to crystallise; on cooling, the crystals, having been by means of pressure separated from the mother-liquor, are mixed with one-fourth of their weight of charcoal powder. They are then heated to 100° in the porcelain or earthenware vessels, so as to obtain a dry mass which admits of being sifted through a copper-wire gauze sieve, after which the material is put into peculiarly shaped retorts and calcined for the purpose of yielding phosphorus. The residue left in the retorts is afterwards calcined with access of air so as to burn off the charcoal, and the remaining phosphate of lime is again treated with strong hydrochloric acid, yielding a concentrated liquor which does not require much evaporation. The phosphorus obtained by this process is refined as already described, the softened bones being treated for glue and size.

Gentele, Gerland, Minary, and Soudry's Methods of Preparing Phosphorus.

According to a communication published by Gentele in 1857, upon a plan of phosphorus manufacture, he combines that industry with the preparation of sal-ammoniac. The bones are treated with hydrochloric acid. To the resulting solution crude carbonate of ammonia is added; this substance being obtained as a by-product of the manufacture of animal charcoal. The phosphate of lime precipitated is employed in the preparation of phosphorus, while the solution of chloride of ammonium is evaporated and sublimed. Gerland (1864) suggests the treatment of bones—first, with an aqueous solution of sulphurous acid, the heating of the liquor obtained with the view of expelling the acid, which being again absorbed by a layer of coke (a coke column such as used in alkali works to absorb hydrochloric acid), the phosphates first held in solution are precipitated by the elimination of the sulphurous acid. Minary and Soudry (1865) proposed to prepare phosphorus from a mixture consisting of phosphate of iron and well-ignited coke.

Properties of Phosphorus.

When perfectly pure and kept under distilled water, which previously to being employed for this purpose has been by boiling deprived of the air it held in solution, and has been cooled either under a layer of oil or in well-stoppered bottles, and in perfect darkness, phosphorus is a colourless and transparent substance; but usually it has a white-yellow colour and waxy appearance. Its sp. gr. is = 1·83 to 1·84. When the temperature of the air is not too low this element is as soft as wax, but becomes brittle in cold weather. Phosphorus cannot be pulverised; is tough; but when molten in a bottle under warm water and shaken until the fluid is quite cold, the substance is thereby reduced to a finely divided state; instead of water it is better to use either alcohol, urine, or a weak aqueous solution of urea. Phosphorus fuses at 44° to 45°, and remains, especially if kept under an alkaline solution, fluid for a considerable time though cooled far below its melting-point, but solidifies suddenly when touched by a solid body. At 290° phosphorus boils, and it evaporates sensibly at the ordinary temperature of the air. By slow oxidation (fumes of phosphorus are given off at the ordinary temperature of the air) there is formed not only phosphorous acid but nitrate of ammonia and antozone. Phosphorus is in the state of vapour slightly soluble in water. The solid element itself is slightly soluble in alcohol and ether, also in linseed oil and oil of turpentine, the best solvents being sulphide or carbon, chloride of sulphur, and chloride of phosphorus. At 75° phosphorus ignites in contact with air, and in order to ignite it by friction this temperature has to be reached. Amorphous or red phosphorus requires a very high temperature (300°) for ignition. Commercial phosphorus usually contains some impurities, such as sulphur, arsenic, and sometimes traces of calcium, due to the lime of the bone-ash used in the preparation. Beside being used in chemistry, phosphorus is chiefly employed in the making of matches; also for what is termed liquid fire (a solution of phosphorus in sulphide of carbon), for the preparation of tar colours, and for hardening some copper alloys.

Amorphous or Red Phosphorus. Dr. Schrötter, of Vienna, discovered in 1848 that the property possessed by ordinary phosphorus (first noticed in 1844 by E. Kopp) of becoming coloured red by the action of light, was due to the formation of an allotropic modification, which has been since termed red or amorphous phosphorus. This is best prepared by heating ordinary phosphorus, with exclusion of air and water, in a closed vessel and under pressure, to 250° for a length of time. On the large scale this operation is conducted in an apparatus invented by A. Albright, of Birmingham. In Fig. 261, *g* represents a glass or porcelain vessel, filled for five-sixths of its capacity with pieces of phosphorus to be heated to 230° to 250°. The vessel *f* is placed in a sand-bath, *b*, heated by the fire. To the vessel *g* is fitted an air-tight lid, into which is fastened the bent tube, *i*, provided with a tap, *k*, and dipping into the vessel *n*, which is filled with water, or preferably with mercury covered with a layer of water. The tap, *k*, is left open at the commencement of the operation for securing the escape of the air contained in *g*, and as soon as no more air escapes the tap is closed, and the heat increased so as to convert the ordinary into amorphous phosphorus. The time required for the operation depends upon conditions which can only be met by experience. After the thorough cooling of the apparatus, the vessel *g* is opened, and the red phosphorus removed. It is then placed under water and crushed to a pulp in order to remove any unconverted ordinary phosphorus. Sulphide of carbon might be used for this purpose, but the danger of ignition (by accident) of the solution of ordinary phosphorus thus obtained is prohibitive. Nicklès proposes to separate ordinary from amorphous phosphorus by shaking up the mixture of amorphous and ordinary phosphorus with a fluid, the specific gravity of which is less than that of amorphous phosphorus (2·1), and greater than that of ordinary phosphorus (1·84). A solution of chloride of calcium at 38° to 40° B. can be used for this purpose; the ordinary phosphorus floats in this fluid and can then be readily taken up by sulphide of carbon, while the operation

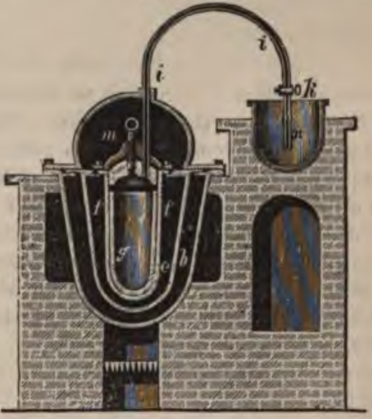


FIG. 261.

can be carried on in a closed vessel. When very large quantities of amorphous phosphorus have to be purified it is best to follow Coignet's plan, consisting in treating the boiling mixture of the two varieties of phosphorus with caustic soda solution, whereby the ordinary phosphorus is converted into phosphuretted hydrogen gas and hypophosphite of soda is formed, the remaining amorphous phosphorus being purified by washing with water. R. Böttger suggests the use of a solution of sulphate of copper, which with ordinary phosphorus forms phosphuret of copper.

Properties of Amorphous Phosphorus. This substance occurs either in powder of a red or scarlet colour or in lumps of a red-brown hue; fracture conchoidal, sometimes with an iron-black hue; sp. gr. = 2·1. Amorphous phosphorus is not soluble in sulphide of carbon or other solvents of ordinary phosphorus. It is unaltered by exposure to air; and when heated to 290° is re-converted into ordinary phosphorus. When mixed and rubbed with dry bichromate of potash red phosphorus does not explode, and when mixed with nitre it does not burn off by friction, but only by application of heat and then noiselessly. It explodes, however, when mixed with chlorate of potash. With peroxide of lead amorphous phosphorus ignites by friction with a slight explosion, but when heat is also applied a violent explosion ensues.

Owing to its properties and behaviour with several oxides, moreover its non-volatility and non-poisonous properties, amorphous phosphorus is, as well as on account of its less ready ignition, an excellent material for the making of matches; but amorphous phosphorus is not in general use for this purpose. It is, however, used for preparing iodide of phosphorus, which serves for the preparation of iodides of amyl, ethyl, and methyl, used in the manufacture of cyanin, ethyl violet, and other coal-tar colours. Sir William Armstrong's explosive mixture for shells contains amorphous phosphorus and chlorate of potash. From 66,000 cwts. of bones there are annually prepared in Europe some 5500 cwts. of phosphorus.

Requisites for Producing Fire.

Generalities and History. According to the writings of the ancients, Prometheus drew fire from stones by their concussion. The Romans rubbed together two pieces of hard wood for producing by friction sufficient heat to ignite dry leaves fallen from trees; while Darwin and the Prince of Neuwied state that the uncivilised races of man obtained fire by the rapid rotation of two pieces of wood. Turners at the present day employ friction in the carbonisation of wood for ornamental purposes. During Titus's reign the Romans obtained fire by rubbing decayed wood between two stones, along with a small thin roll of sulphur. In the fourteenth century, the tinder-box, with the flint and steel, became known, and also the so-called German tinder, a prepared cryptogamic plant. Till 1820 these remained generally the chief means of obtaining fire, aided, of course, by the wooden splints tipped with sulphur.

In the year 1823, Döbereiner, at Jena, discovered that finely divided spongy platinum has the property of igniting a mixture of atmospheric air and hydrogen gas, and he contrived the so-called Döbereiner hydrogen lamp, which has been, and is still, occasionally employed to procure fire and light. About the same period there was invented a kind of phosphorus match of the following arrangement. Equal parts of sulphur and phosphorus were cautiously fused in a glass tube; after the fusion was completed the tube was tightly corked. If it were desired to obtain fire, a thin splint of wood was immersed in this mixture, and some of it having been fixed to the wood, the latter on being brought into the air became ignited by the combustion of the mixed substances, which took fire spontaneously in the air. It is evident that this rather clumsy contrivance never became general. Of far more importance as suited for practical purposes were the chemical matches or dip splints, first manufactured at Vienna, as early as 1812. These splints were tipped with sulphur covered with a mixture of chlorate of potash and sugar, to which for the purpose of imparting colour was added some vermillion, while a little glue gave a pasty and adhesive consistency.

By touching this composition with concentrated sulphuric acid ignition ensued; the acid was kept in a small glass or leaden bottle into which some asbestos had been inserted, which acted as a sponge for the acid. The only friction matches known up to the year 1844 were discovered and made by M. Chancel, assistant to the well-known Professor Thenard of Paris, 1805. The *Prometheans*, first made in England in or about the year 1830, were contrived on the same principle, viz., the ignition by friction between two hard substances of a mixture of chlorate of potash and sugar fixed to a kind of paper cigarette, which contained also a small glass globule filled with sulphuric acid; however, the high price of this kind of match prevented its general use. Under the name of Congreves the first real friction matches were made in 1832. On the sulphur-tipped splints was glued a small quantity of a mixture of 1 part of chlorate of potash and 2 parts of black sulphuret of antimony, to which some gum or glue was added. By strongly pressing this composition between two pieces of sand-paper the mixture became ignited, but frequently also on becoming detached from the wooden splint flew about in all directions without igniting the sulphur or the wood. It is not well known who was the first to substitute phosphorus for sulphuret of antimony; but according to Nicklès phosphorus matches were already in use in Paris as early as 1805, while in 1809 Derepas proposed to mix magnesia with phosphorus in order to lessen its great inflammability when in finely divided state. Derosne (1816) appears to have been the first who made phosphorus friction matches at Paris. However, it was not before the middle of 1833 that phosphorus matches became more generally known, when Preshel, at Vienna (this city is famous for the match and fusee industry in Germany), made not only phosphorus matches, but also fusees and German-tinder slips tipped with the phosphorus composition. About the same period F. Moldenhauer, at Darmstadt, made phosphorus lucifer matches. The South Germans attribute to Kammerer the invention of phosphorus lucifer matches, while in England, according to the opinion of the late celebrated Faraday, John Walker, of Stockton, Durham, was the inventor of lucifer matches, or at least the first maker. The older kind of matches, although very combustible, ignited with a rather sharp report, owing to the presence of chlorate of potash in the mixture, while, moreover, the too ready ignition by concussion rendered the transport of these matches so unsafe, that in Germany, the transport, as well as the manufacture, became prohibited. In the year 1835 Trevany substituted a mixture of red-lead and manganese for a portion of the chlorate of potash, thereby greatly improving the composition. In 1837 Preshel altogether discarded this salt, substituting peroxide of lead, or, as Böttger advised, either a mixture of red-lead and nitrate of potash, or of peroxide of lead and nitrate of lead. From this period the manufacture of matches became an extensive industry, greatly aided by the manufacture of phosphorus on the large scale.

In the course of time other improvements were made, as, for instance, the substitution for sulphur of wooden splints, thoroughly dried and soaked in wax, paraffin, or stearic acid, the coating of the composition with a varnish to protect it from the action of moisture, while, at the same time, the external appearance of the matches was rendered more ornamental. At the present day matches are a product of an industry which cannot possibly be much more improved in a technical point of view, being also a product which, as regards its price, is within the reach of all.

However useful phosphorus lucifer matches may be, it is a great drawback to their utility that the combustible composition is a poisonous mixture, while, moreover, the workpeople engaged in that department of the lucifer-match making in which the phosphorus is handled are often affected by a peculiar kind of caries of the jaw-bones, the real cause of which is the more difficult to ascertain as the workpeople engaged in the manufacture of phosphorus and exposed to its vapours to such an extent as to render their breath luminous in the dark are not similarly affected. The discovery of the red or amorphous phosphorus, which is neither poisonous nor very inflammable, affords a happy substitute for the ordinary phosphorus, but the former is by no means generally used in the preparation of matches.

Manufacture of Lucifer Matches. The operations required are:—

1. The preparing of the splints of wood.
2. The mixing of the combustible composition.
3. The dipping, drying, and packing of the matches.

1. *The Preparation of the Wooden Splints.*—Generally white woods are used for this purpose, such as white fir, pine wood, aspen, more rarely fir wood (Föhrenholz), sometimes beech wood, lime-tree wood, birch, willow, poplar wood, and cedar. The shape of the splints is usually square in section, but abroad the splints are sometimes cylindrical. The square splints are readily made by hand, simply by splitting up a block of wood having the length required for the splint. A cutting tool, a large knife, similar to that which is sometimes used by chaff-cutters, is very frequently used for the purpose of cutting the wooden splints, while a contrivance similar to that in use for propelling the hay or straw forward is also employed, being so arranged as to propel the wood after every cutting stroke the length required for a splint. More generally the operation of splitting the block of wood parallel to its fibres and next cutting off the splints to the required length is effected by machinery consisting of fixed knives, against which the wood is moved with sufficient force to split it up into splints, which are next cut to the required length. Instead of splitting the wood by these means, the splints are now in Germany always made by a kind of plane, invented by S. Romer, of Vienna, by which the wood is cut up into circular splints. The cutter of this plane differs from that of the ordinary carpenter's plane, by possessing, instead of the cutting edge, a slight bend, in which three to five holes have been bored in such a manner that one of the edges of these holes is sharpened; in practice three holes are preferred. When this plane is forced against a lath of wood, placed edgeway, the cutting tool penetrates into the wood, splitting it up into as many small sticks or splints as the cutter contains holes. When a number of thin splints have been cut from the lath, it is again planed true with an ordinary plane and then the operation repeated. The dividing of the thin sticks into splints of the required length is effected by a tool consisting of a narrow trough about 6 centims. wide and provided with a slit in which works a knife fastened to a

lever. A clever workman can prepare 400,000 to 450,000 splints daily. In the south-west of Germany a plane for cutting wooden splints, the invention of Anthon, at Darmstadt, and similar in action and construction to that above mentioned, is in general use; but throughout an extensive portion of the empire the manufacture of the splints has become a separate trade often carried on in woods and forests, the splints being sold to the lucifer-match makers in bundles ready for dipping.

Instead of making the splints by hand they are occasionally made by a machine, such as that by Pellitier, at Paris (1820), having on a bench a plane 36 centims. long by 9 wide, made to move backwards and forwards, while a piece of wood is placed so that it is caught by the fore-cutter, which consists of a steel knife provided with twenty-four teeth sharpened like little knives, the second cutter removing the small laths from the plank of wood. Cochot's machine (1830) consists of a large iron wheel 1 metre in diameter, on the periphery of which are fixed thirty wooden blocks lengthway of the size of the splints. When the wheel is turned round the blocks of wood are caught by the knives fastened to a small cylinder, and the wood is split up into splints, which are removed from the block by another knife. Jeunot's machine, patented in 1840 in France, is of a similar construction. Neukrantz, at Berlin (1845), contrived a tool based upon the principle of the hand-plane, the wood intended to be cut being moved against a fixed steel cutter, which produced sixteen to twenty splints at a movement. Krutzsch, at Wünschendorf, Saxony, has improved upon this plan (1848) by perforating a steel plate with about 400 holes placed as near together as possible; the edges of these holes having been sharpened, a block of wood is forced in the direction of its fibres against the plate and thus divided into splints. A piece of wood 3 centims. in thickness and width by 1 metre in length yields 400 lengths, each of which can be cut up into fifteen splints; 6000 of the latter are made in two minutes. Of the several tools and machines contrived for the purpose of cutting splints—and the number of these contrivances is very large—we quote the following of German origin. The machine invented by C. Leitherer, at Bamberg (1851), consists of what might be termed a kind of guillotine, viz., a box at the bottom of which is placed the wood to be formed into splints, the fibre of the wood being vertical. In front of this box is placed a frame-work, in which a heavy block, provided with four cutters, each terminated by eight to ten narrow tubes (somewhat similar to cork-borers), can be made to move rapidly, so as to give forty-five strokes a minute, the wooden block intended to be cut into splints being made to move under the cutting tool after each stroke. Wrana's machine is in principle the same as that of Neukrautz, but has been greatly improved, the plane not being fixed, but supported by a piece of wood. Long's machine, again, consists of a series of cylinders, between which the block of wood is placed, while knives are so arranged as to cut the block into splints while the wood moves on by the motion imparted to the cylinders.

2. *The Preparation of the Combustible Composition* is carried on in the following manner:—The glue, or gum, or any other similar substance, is first dissolved in a small quantity of water to the consistency of a thin syrup, with which, having been heated to 50°, the phosphorus is incorporated by gradually adding it and keeping the mixture stirred so as to form an emulsion, to which are next added the other ingredients after having been pulverised. In order to obtain a good composition, it is essential that there should be neither too much nor too little phosphorus, for an excess of phosphorus will not only tend to increase unnecessarily the price of the

composition, but it has also the effect of rendering it unfit for igniting the sulphur and stearin wherewith the matches are tipped, because the phosphoric acid generated by the combustion of the phosphorus is deposited as an enamel-like mass, which prevents further combustion. It appears that the best proportion is from one-tenth to one-twelfth of phosphorus.

A much smaller quantity of phosphorus is required if this element is first dissolved in sulphide of carbon and the solution added to the other constituents of the composition; the sulphide of carbon while rapidly volatilising leaves the phosphorus in a very finely-divided state. As phosphorus is very readily soluble in sulphide of carbon, and as the latter is moderately cheap, the method has the advantage that the mixing of the materials can take place without the application of heat. It is, however, evident that the greatest care is required in manipulating such a liquid as sulphide of carbon, and far more when phosphorus is dissolved therein. C. Puscher suggested (1860) the use of sulphuret of phosphorus, P_2S, instead of pure phosphorus in the composition for matches. He prepared a composition containing 3·5 per cent of this sulphuret, and obtained excellent matches.

Among the metallic oxides which are employed in the mixture, preference is given either to a mixture of peroxide of lead and nitrate of potash, or to a mixture of the former with nitrate of lead obtained by treating red-lead with a small quantity of nitric acid and leaving this mixture for a period of several weeks to dry. Glue, gum, and dextrine are used as excipients; the first, however, is objectionable because it carbonises and prevents the combustion. Perhaps a dilute collodion solution or a mixture of sandarac or similar resin, with benzole, might be used as an excipient instead of the gum.

The mixtures actually used in the trade are kept secret, but the following recipes may give some idea of the composition:—

I.

Phosphorus	1·5 parts	
Gum senegal	3·0 „	
Lamp-black	0·5 „	
Red-lead	5·0 „	A mixture of nitrate of lead and of peroxide of lead, technically known as oxidised red-lead.
Nitric acid at 40° B. (= sp. gr. 1·384)	2·0 „	

II.

Phosphorus	8·0 parts	Dissolved in the required quantity of sulphide of carbon.
Glue	21·0 „	
Peroxide of lead	24·4 „	
Nitrate of potash	24·0 „	

III.

Phosphorus	3·0 parts
Gum senegal	3·0 „
Peroxide of lead	2·0 „
Fine sand and smalt	2·0 „

No doubt there is room for great improvements in these compositions.

3. *Dipping and Drying the Splints.*—In order to fix the sulphur and combustible composition to one end of the splints, it is clear that these should not touch each

other, but be so arranged as to leave an intermediate space. A contrivance is employed, consisting of small planks, 0·3 metre long by 10 centims. wide, the surface being provided with narrow grooves placed close together, and just large enough each to hold a single splint, Fig. 262. The splints are one by one placed in the grooves, an operation usually performed by girls. One plank having been filled another is placed on the top of it. The surface of the plank on one side is provided with a piece of coarse flannel, while the other side is grooved for holding splints. Each of the planks has at the end a round hole, through which pass iron rods, Figs. 263 and 264, in the top of which a screw thread is cut, so that as soon as some twenty to twenty-five planks have been filled with splints and placed one upon another, they are fastened so as to form a framework. A clever hand can fill during ten hours fifteen to twenty-five of these frames, each containing 2500 splints. Recently it has been attempted to perform this work by machinery, and the machine constructed by O. Walsh, at Paris (1861), enables a lad to frame 500,000 to 600,000 splints in ten hours.

The sulphur intended for dipping the splints is kept in a molten state over a moderate fire in a shallow rectangular trough, in the middle of which a stone is placed as precisely level as possible. The quantity of sulphur is so regulated that it covers the stone to a depth of 1 centim. In the operation of dipping, the ends of the splints are made just to touch the stone and immediately removed, care being taken to cause, by shaking the frame, any superfluous sulphur to flow into the trough again.

FIG. 262.

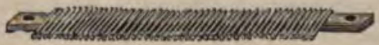


FIG. 263.

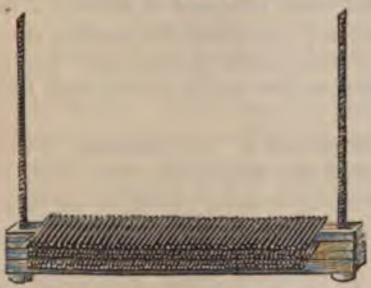
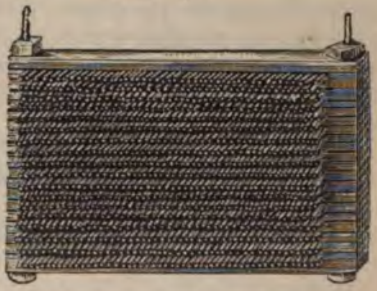


FIG. 264.



Instead of sulphur the better kind of matches are impregnated with stearine, stearic acid, or paraffin. The splints having been first thoroughly dried, are placed in a bath of molten paraffin, and left there for a time so as to allow the wood to absorb by capillarity.

The tipping with the phosphorus composition is performed similarly to the sulphuring of the splints, the composition being placed in a uniform layer on a piece of thick ground glass or on a well-polished lithographic stone (Solenhofen limestone).

The drying of the matches takes place in a room heated by steam, the frames being hung on ropes or put on shelves. The position of the frames is such that the matches are in a vertical position, and the composition hangs on them as a drop. The composition of the saloon matches is, after drying, coated with coloured resinous solutions, and often with a collodion film.

Anti-Phosphor Matches. This variety of match was invented in 1848, by Böttger, at Frankfort, and was prepared industrially by Fürth, at Schüttenhofen; Lundström, at Jönköping (Sweden); Coignet, at Paris (under the name of *Allumettes hygiéniques et de sureté au phosphore amorphe*); De Villiers and Dalemagne, Paris (under the name of *Allumettes androgynes*); also by Forster and Wara. These matches are of two kinds:—α. Those which are free from phosphorus, the amorphous phosphorus being incorporated with the sand-paper. β. Those which are free from phosphorus both in the match and on the sand-paper.

To the matches of the first category belong:—1. Matches, the composition of which is free from phosphorus, consisting simply of a pasty mass, the main constituents of which are sulphuret of antimony and chlorate of potash. 2. The amorphous phosphorus mixed with some very fine sand or other substance promoting friction is, with glue, put on to the box in which the matches are contained; or, as is the case with the *androgynes*, at the other end of the splint. The friction surface on the boxes consists of a mixture of 9 parts of amorphous phosphorus, 7 parts of pulverised pyrites, 3 parts of glass, and 1 part of glue. The matches ignite readily by friction on the surface containing this composition, but do not ignite when rubbed on any other rough surface. These so-called safety matches are largely manufactured at Jönköping, under the Swedish name of *Sakerhets-Tändstickor* (security fire matches). Jettel (1870) uses for the friction surface a compound consisting of equal parts of amorphous phosphorus, pyrites, and black sulphuret of antimony; for coating on the two sides of 1000 small boxes, each containing fifty matches, about 80 grms. of this mixture are required. It need hardly be mentioned that in England safety matches are largely made and of excellent quality, in fact, better than anywhere else.

B. Forster and F. Wara, at Vienna, have introduced a "non-poisonous" match. The amorphous phosphorus is mixed up with the combustible composition in the usual way, so that these matches ignite readily by being rubbed on any rough surface, but the ignition is accompanied by noise, owing to the chlorate of potash contained in the mass.

As regards the matches belonging to the second category—viz., such as neither contain phosphorus nor require a phosphorus-containing surface, we may give the analysis by Wiederhold, of the composition of those made by Kummer and Günther, at Königswalde, near Annaberg, in Saxony:—

Chlorate of potash	8 parts.
Black sulphuret of antimony	8 „
Oxidised red-lead	8 „
Gum senegal	2 „

Oxidised red-lead is a variable mixture of peroxide of lead, nitrate of lead, and undecomposed red-lead. Weiderhold, at Cassel, suggested (1861) the following ignition mixture:—

Chlorate of potash	7·8 parts.
Hyposulphite of lead	2·6 „
Gum arabic	1·0 „

This is the best anti-phosphorus mixture. Jettel, at Gleiwitz, gives the following mixtures free from phosphorus:—

	a.	*b.*	*c.*	*d.*
Chlorate of potash	4·0	7·0	3·00	8·0
Sulphur	1·0	1·0	—	—
Bichromate of potash	0·4	2·0	—	0·5
Sulphuret of antimony	—	—	—	8·0
Sulphur auratum, SbS_5 (Stibium sulfuratum aurantiacum). (Antimonium sulfuratum, B.P.)	—	—	0·25	—
Nitrate of lead	—	2·0	—	—

While R. Peltzer has called attention to the applicability of copper-sodium hyposulphite for the preparation of a phosphorus-free ignition mass, Fleck* has also remarked the use which might be made of sodium in this respect.

Wax or Vesta Matches. Instead of the phosphorus composition being fixed to a wooden splint it is in the wax matches (*allumettes bougies*) attached to a thin taper made of a few cotton threads (4 to 6), immersed in a molten mixture of 2 parts of stearine and 1 part of wax or paraffin. The tapers, while this mixture is hot, are drawn through a hole perforated in an iron plate, the opening of which corresponds to the desired thickness of the taper. The taper is next cut by means of machinery into suitable lengths; afterwards the phosphorus composition is affixed and the vestas put into boxes.

Zulzer's machine for cutting the tapers and for making them into matches has the following arrangement. The wicks having been rolled on a drum are forced between two cylinders, which impart the fatty composition, and next the tapers are carried by the machinery across grooves in planks to holes in a movable vertical iron plate, which is connected with a cutting apparatus intended to divide the tapers into suitable lengths. As the cutters are placed at the entrance of the holes, the tapers after having been separated from the main wicks are left dangling in these holes, and by a mechanical contrivance, the plate containing the holes is lifted sufficiently to bring another row of holes level with the wick-producing apparatus. When a plate has been thus filled with tapers it is removed, another put in its place, and the ends of the tapers immediately immersed in the phosphorus composition, and next placed in a drying room. Marseilles is the great centre of the wax match industry, while Austria stands next.

ANIMAL CHARCOAL.

Animal Charcoal. Animal charcoal is the residue obtained by the dry distillation of bones. Owing to its introduction (1812) by Derosne, and afterwards re-introduction with improved filtering apparatus by Dumont (1828), into the sugar refining industry, animal charcoal, or bone-black, has become one of the most important substances of chemical technology. When bones are submitted to ignition in closed vessels with exclusion of air, the organic matter yields a tar known as crude Dippel's oil, and carbonate of ammonia, while a coal-black residue remains exhibiting perfectly the organised structure of the bones.

Preparation of Bone-black. The bones are either boiled with water or, better, exhausted with sulphide of carbon to remove the fat, which being obtained in a quantity of 5 to 6 per cent of the weight of the bones, is a valuable by-product of this branch of industry. The carbonisation of the bones is so conducted that the volatile products are either burnt or condensed. In the latter case the broken-up bones are put into iron retorts similar to those used for coal-gas manufacture, and the volatile products are collected in suitable condensing apparatus, while the gas after having been purified is sometimes led into a gasholder and used for illuminating purposes, or when not purified is burnt under the retorts. According, however, to the experience obtained in Germany, bone-black thus made has a lower decolourising power than when the bones are ignited in iron pots, the volatile products being burnt at the same time. In Germany, therefore, the older plan of carbonisation in pots is usually resorted to. In England and Scotland, and also in Holland, Belgium, and France, retorts are generally used for this purpose. The carbonisation in pots is carried on in the following manner:—Cast-iron pots are filled with broken-up bones and placed one on the top of the other, the edges of the mouths of the pots being luted with clay. The pots are placed on the hearth of a kind of reverberatory furnace. After awhile the vapours which are forced through the lute become ignited, thereby enveloping the pots in a sheet of flame, so that the carbonisation goes on without requiring the firing of the furnace to be kept up. When the flame subsides the carbonisation is complete. The yield of animal charcoal amounts by this method of procedure to 55 to 60 per cent, the carbonaceous matter being, however, mixed with about ten times its weight of mineral matter, as may be inferred from the following results of analysis of a dried sample of bone-black, which in 100 parts was found to consist of—Carbonaceous matter, 10; phosphate of lime, 84; carbonate of lime, 6 parts. By exposure to air bone-black absorbs 7 to 10 per cent of moisture. The carbonised bones are broken up and granulated by machinery, the formation of dust having to be avoided as much as possible because it has very little value.

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* Jahresbericht der Chem. Technologie (Dr. Wagner), 1868, p. 220.

Properties of Bone-black. As far back as the year 1811, Figuier discovered that bone-black possesses the property of withdrawing organic and inorganic substances—viz., lime and potash from solutions. It appears that this property is due to surface attraction (capillary action), although bone-black is also capable of decomposing chemical compounds. Owing to the fact that bone-black can absorb inorganic matter, it is largely used for the purpose of withdrawing lime and saline matter from saccharine fluids in beet-root sugar works. According to Anthon, the property of bone-black to withdraw lime from solutions is partly due to the fact that carbonic acid is condensed in the pores of this substance.

By treating bone-black with hydrochloric acid, and thus dissolving the mineral matter it contains, the residue, after having been well washed with water, dried, and re-ignited in a closed crucible, has lost in a very great measure its property of withdrawing from solutions and retaining within its pores inorganic matter. When acid liquids are to be decolourised by bone-black, it should always be employed after having been treated with hydrochloric acid. Shoe-blacking manufacturers employ in their trade a large quantity of bone-black.

Testing Bone-black. The greater the decolourising power of charcoal the better its quality, though it appears that the decolourising power is not proportionate to the power of withdrawing lime and saline matters from solutions. In order to ascertain the decolourising power of any sample of bone-black, its quality in this respect is compared with that of another of known strength. Payen proposes to take equal bulks of water coloured with caramel, to treat these with equal weights of animal charcoal, and to filter these mixtures; the charcoal which yields the clearest liquid being the best. Bussy obtained the following results by the estimation of the relative decolourising power of equal quantities by weight of different kinds of charcoal:—

Ordinary bone-black	1·0
Bone-black treated with hydrochloric acid	1·6
Ditto, ditto, but afterwards ignited with carbonate of potash	20·0
Blood ignited with carbonate of potash	20·0
Blood ignited with carbonate of lime	20·0
Glue ignited with carbonate of potash	15·5

Brimmeyr's experiments on the decolourising properties of bone-black led to the following results:—1. The capability of absorption of this substance does not depend upon the mechanical structure of the bone-black, but upon the quantity of pure carbon it contains. 2. The quantities of matter absorbed by bone-black of various kinds are—when reduced to pure carbon—really equivalent, and are probably independent of the varying chemical nature of the soluble absorbed substance. 3. Bone-black saturated with any substance retains its absorptive power for other materials of a different chemical nature. 4. Bone-black acts the quicker and better the less its capillary structure has been interfered with either by mechanical or chemical means (action of hydrochloric acid). Schultz's results of experiments agree with those just quoted. The specifically lightest bone-black which contains the largest amount of carbon is the most strongly decolourising material. As regards the sugar (especially beet-root) manufacture, the power of bone-black to withdraw lime from a solution comes also into consideration; this lime-absorbing capability is estimated by directly testing the quantity of lime which a given sample of charcoal can take up.

Revivification (Re-burning) of Charcoal. After having served the purpose of decolourising and absorbing lime for some time in the process of sugar refining, the bone-black becomes, as it is termed, foul and requires to be revived, for which purpose it is either first thoroughly washed with hot water or sometimes left to enter into a state of fermentation, or treated with steam, and finally always re-ignited. The more usual plan is to wash the bone-black, while still in the filters, with hot water, so as to remove all soluble matter, the material being next re-ignited. In this manner bone-black may be restored for use twenty to twenty-five times. This mode of reviving labours under the disadvantage that during the ignition the organic matter (absorbed impurities) is not quite destroyed, and by choking the pores of the bone-black impairs its decolourising power. It is therefore preferable to cause the bone-black to ferment, to treat it next with dilute hydrochloric acid, wash it well, and lastly ignite it. The quantity of hydrochloric acid employed for this purpose in sugar-producing works is very large.

Substitutes for Bone-black Among the substances which have been tried as substitutes for the use of bone-black, carbonised bituminous shale takes the first place. This material (the coke of the Boghead coal is an excellent example) absorbs colouring matter, but does not touch the lime. Moreover it often happens that the coke is rendered unfit for this use by the presence of a considerable amount of mono-sulphuret of iron. The coke of sea-weed is perhaps a more suitable material.

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MILK.

MILK. This fluid is secreted by glands with which all female mammalia are provided. It contains all the organic and inorganic substances required by the young animal as food, being intended to feed the young until they are sufficiently developed to partake of other nutriment. The main constituents of milk are:—Sugar (lactose), caseine, butter, inorganic salts, such as chlorides of potassium and sodium, phosphate of lime, and finally water. The average percentage composition of cow's milk is the following:—

Butter	3·288	12·524 per cent.
Lactose and soluble salts ...	5·129	
Caseine and insoluble salts ...	4·107	
Water	87·476	
	100·000	

Milk is a mixture of several insoluble, very minutely divided, emulsioned substances, suspended in a watery liquid. The specific gravity of milk varies from 1·030 to 1·045. Under the microscope it becomes evident that the white colour of milk is due to the so-called milk globules—small globular bodies of a yellow colour, with a more deeply coloured circumference, and exhibiting a pearly gloss. It was formerly believed that these globules consisted of an exterior envelope filled with butter, but the recent researches of Drs. Von Baumhauer and F. Knapp have proved this opinion to be erroneous. When milk is left standing these globules rise to the surface and form cream, below which remains a blue transparent fluid containing the sugar of milk, salts, and caseine, the latter in the form of caseine-soda When milk is kept for some time a portion of the lactose (sugar of milk) is decomposed and converted into lactic acid by the aid of the caseine, which acts as a ferment. In its turn the lactic acid decomposes the caseine-soda, whereby the caseine is set free and separated as an insoluble substance; this action takes place in the coagulation of milk. The whole of the lactose or sugar of milk becomes converted into lactic acid by long keeping.

Lactic acid ($C_3H_6O_2$) is also formed by the fermentation of starch, cane sugar, and glucose, under the influence of caseine and a ferment. This acid is met with in sauerkraut (a favourite dish of the Germans, being a well-preserved mixture of white and savoy cabbages cut into shreds, and packed in casks along with salt, coarse pepper, and some water), and in other pickles, in beer, and in nearly all animal liquids. Lactic acid is also present in some of the fluids of the tan-yard tanks; in the sour water of starch works where starch is prepared by the old methods; in the bran bath of dye works; and is constantly met with in the residual liquids of corn spirit distillation. When lactic acid is heated with sulphuric acid and peroxide of manganese, aldehyde is formed, which is used in the preparation of aniline green and of hydrate of chloral.

The coagulation of fresh milk is effected by the use of rennet, which is prepared from the stomach of a calf, well washed and stretched out in a wooden frame, then dried either in the sun or near a fire. The substance thus prepared was formerly soaked in vinegar, but experience has proved this to be unnecessary. When required a small piece is cut off and steeped in warm water, and the liquid added to the milk previously heated to 30° to 35°. The milk is hereby coagulated, even in large quantity, in about 2 hours; 1 part of rennet is sufficient for the purpose of coagulating 1800 parts of milk. The mode of action of rennet is not well understood, but it does not consist, as was formerly believed, in the instantaneous conversion of a portion of the lactose present in milk into lactic acid, since experiments have shown that rennet coagulates milk which exhibits an alkaline reaction.

Whey. By the term whey is understood the fluid in which the coagulated caseine of milk floats and which may be obtained either by decantation or filtration. The whey of sour milk contains very little lactose and a large quantity of lactic acid (sour whey); while sweet whey, obtained by coagulating milk with rennet contains all the lactose. Sweet whey containing 3 to 4 per mille of a proteine compound (termed lacto-proteine by Millon and Commaille) is evaporated to some extent in Switzerland, with the view of obtaining the sugar of milk in crystalline state. **Lactose—Sugar of Milk.** The substance thus obtained is purified by re-crystallisation. Lactose, $C_{12}H_{22}O_{11} + H_2O$, does not possess a very sweet taste and feels sandy in the mouth. It is soluble in 6 parts of cold and 2 parts of hot water. It is not capable of alcoholic but only of lactic acid fermentation. By the action of dilute acids sugar of milk is converted into galactose, a kind of sugar similar to grape sugar, and is then capable of alcoholic fermentation. Industrially sugar of milk is sometimes employed for the purpose of reducing a silver solution to the metallic state, as in the case of looking-glass making. 100 parts of the commercial sugar of milk from Switzerland (*a*), and from Giesmannsdorf in Silesia (*b*), were found to consist (1868) of:—

	a.	*b.*
Salts	0·03	0·16
Insoluble matter	0·03	0·05
Foreign organic substances...	1·14	1·29
Sugar of milk	98·80	98·50
	100·00	100·00

Means to Prevent Milk becoming Sour. By boiling milk the air it has taken up is eliminated and thereby the conversion of the caseine into a ferment, and the consequent decomposition of the sugar of milk, prevented. Milk may very readily be kept fresh by the addition of small quantities of carbonates of alkalies or borax. The coagulation of milk (not its becoming sour) may be prevented by the addition of some nitrate of potash, chloride of sodium, or other alkaline salts.

Testing Milk. In localities where milk is consumed in very large quantities—for instance, in large cities and towns—it is sometimes adulterated by the addition of rice-water, bran-water, gum-solution, and emulsion of sheep's brain. The most common adulteration of milk is its dilution with more or less water. Several methods and instruments have been invented for the purpose of testing the quantity of caseine and butter present in milk, and it should be here observed that, according to Dr. F. Goppelröder's excellent researches (1866), it has been found that the relative proportion of the quantity of these substances varies in milk from one day to another, and even in the milk drawn at mornings and afternoons. According to Jones's plan milk is poured into a vertical graduated glass tube; the quality of the milk varies with the number of graduated divisions occupied by the cream separated from the milk. It is evident that in this way only the quantity of cream contained in the sample of milk under examination is found, and nothing learnt about the degree of dilution of the milk with water, which somewhat influences the rapidity of the separation of the cream. Chevalier and Henry employ for the testing of milk an areometer, the degrees of which are ascertained by experiment from really genuine milk. Other methods are based upon the use of tincture of nut-galls or solution of sulphate of zinc for the purpose of precipitating caseine and butter in a sample of genuine milk, and next to compare the quantity of these reagents necessary to precipitate in an equal quantity by bulk of any other sample of milk. Donné's galactoscope may be used for the purpose of testing the purity of milk, more especially in reference to its adulteration with water, the instrument being based upon the greater or less transparency of a column of milk of a certain length which admits through it the rays from the flame of a lighted candle; the more transparent—that is, the longer the column of milk—the more it is adulterated with water. Brünner tests milk in the following manner:—To 20 grms. of the milk to be tested are added 10 grms. of charcoal powder. This mixture is evaporated to dryness at a temperature of 70° to 80°. The butter is then extracted by means of ether, and this solution evaporated and weighed. Pure milk yields 3·1 to 3·56 per cent of butter, cream from 10·6 to 11·06 per cent. C. Reichelt has lately tried to apply the hallimetrical method (see p. 422) for the purpose of determining the quantity of water contained in milk.

Uses of Milk. Milk is used as food and for the preparation of butter and cheese, for clarifying wine in order to render it less deep coloured, and, if turbid, quite clear. More recently milk has been largely sold in the so-called condensed state, by which is understood milk evaporated *in vacuo* after the addition of sugar to the consistency of thick honey. This mode of preserving milk was first employed by the Anglo-Swiss Condensed Milk Company at Cham, Canton Zug, Switzerland, and is now carried on in various parts of the Continent and in the United States, and also in England, in Surrey and Berkshire. The average composition of the condensed milk is:—

Water	22·44
Solid matter	77·56
	100·00

One-half of the solid matter consists of the sugar which has been added, the rest being butter, 9 to 12 per cent; caseine and lacto-proteine, 12 to 13 per cent; sugar of milk, 10 to 17 per cent; salts, 2·2 per cent. Condensed milk is soluble in cold water, and yields with 4·5 to 5 parts of water a liquid similar to genuine, but of course sweetened, milk.

Butter. This substance is prepared as follows:—Milk of good quality is placed in a rather cool cellar or other locality for the purpose of causing the cream to separate. The cream is poured into a clean stoneware or glass vessel kept for the purpose, and left until by constant stirring it has become thick and sour; it is then put into a churn, by the action of which the solid fat globules are separated from the thick fluid in which the caseine with a small quantity of butter remains suspended. Butter being specifically lighter than water should, it might be thought, separate very readily from a liquid which contains in solution various substances which are heavier; but the fact is, that caseine renders the separation of butter from cream difficult even when the cream is sweet and not thick; when, on the other hand, milk coagulates before the cream is separated, the butter is lost. Two methods have been devised for the purpose of obtaining all the butter contained in milk. Gussander, a

Swedish agriculturist, has proposed that the separation of cream should be rendered more rapid, and always completed before the milk becomes sour, while Trommer prevents the souring of the milk by the addition of some soda.

The churns vary very much in construction; the most simple, which is that most extensively used, consists of a tall somewhat conical wooden vessel covered with a wooden lid, through a round opening in which a cylindrical wooden stem passes. To this stem is fixed a wooden perforated disc, which is moved upwards and downwards by a similar motion imparted to the stem. The butter having been separated from the liquid is thoroughly washed and kneaded with fresh water, and next more or less salted, at least in most cases, although thoroughly well-washed butter may be kept for a very long time without becoming rancid. The liquid from which the butter is separated is known as churn-milk or buttermilk; it contains 0·24 per cent butter, 3·82 per cent casein, 90·80 per cent water, 5·14 per cent sugar of milk and salts. In the water lactic acid is present. 18 parts of milk yield on an average 1 part of butter, which in fresh condition consists of:—

	I.	II.	III.	IV.
Butter fat	94·4	93·0	87·5	78·5
Caseine, sugar of milk Extractive matter ...	0·3	0·3	1·0	0·3
Water	5·3	6·7	11·5	21·2

Owing to the presence of water and caseine, butter after some time becomes rancid. It is salted in order to prevent this rancidity as much as possible, the salt being thoroughly mixed with the butter by kneading. To 1 kilo. of butter 30 grms. of salt are required. According to Dr. Wagner, butter in England is salted with a mixture of 4 parts of common salt, 1 part of saltpetre, and 1 part of sugar. In Scotland, France, Southern and Western Germany, butter is not salted at all, and therefore only made and sold in comparatively small quantities at a time. Salt butter is termed in Scotland pounded butter.

By melting butter until the first turbid liquid has become clear and oily, water and caseine are eliminated, and settling to the bottom of the vessel, the supernatant fat may be put into another vessel, and will, after cooling, keep sweet without salt for any length of time. Butter is often artificially coloured either by the aid of annatto, turmeric, or infusion of calendula flowers.

Chemical Nature of Butter. Butter consists of a mixture of neutral fats—glycerides—which on being saponified yield several fatty acids, among which the non-volatile are:—Palmitinic acid, $C_{16}H_{32}O_2$, and butyroleic acid ($C_{12}H_{30}O_2$). The volatile are:—Butyric acid[*] ($C_4H_8O_2$), capronic acid ($C_6H_{12}O_2$), caprylic acid ($C_8H_{18}O_2$), caprinic acid ($C_{10}H_{20}O_2$). The last four constitute in the shape of glycerides the butyrin or peculiar fat of butter, and impart to that substance its peculiar odour and flavour.

Cheese. Cheese is prepared from caseine. It is made either from skimmed or unskimmed milk. In the former case a lean, dry cheese is obtained; in the latter a fat cheese, such as Cheshire, Cheddar, American, and the bulk of Holland cheeses. Lean cheese is made in Germany by pouring the skimmed and already sour milk upon a cloth, through the pores of which the whey passes, while the caseine remains on its surface as a pasty mass, which is put by hand into the cheese-moulds, these being next exposed to air.

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[*] This acid is formed not only by the saponification of butter, but is also met with in secreted perspiration, the juices of the stomach, and results from the fermentation and decay of sugar (in weak solutions), starch, fibrine, caseine, &c.

Fat cheese is made of sweet milk just drawn from the cows, the milk being coagulated by rennet after having been heated to 30° to 40°. The gelatinous mass thus obtained is broken up and pressed by hand, and the whey gradually removed by the aid of wooden ladles. The caseine having been freed from whey is next well kneaded with some common salt and then put into wooden moulds with two or three small holes at the bottom for the purpose of allowing the whey to flow off when the cheese is pressed. The newly made cheese is usually every alternate day dipped in warmed whey, next wiped dry, put into the mould again, and pressed. When the crust has sufficiently formed and the cheese become so hard as to admit of being handled, some salt is rubbed into its surface and it is then placed in a cool well-aired room upon a shelf to dry, and become as it is termed ripe. The vesicular appearance of some kinds of cheese (the Gruyère cheese exhibits this in a high degree) is indirectly due to the incomplete removal of the whey, the sugar contained becoming during the ripening converted into alcohol and carbonic acid, which by its expansion while escaping produces the vesicular texture. Dutch cheese does not exhibit this appearance on account of being strongly pressed and containing much salt, by which the fermentation of the sugar of milk in the cheese is prevented. The quality of the cheese depends to some extent upon the temperature of the room in which it ripens. At Allgäu 1 cwt. of Swiss cheese of the first quality is produced from 600 litres of milk, while for the second quality 720 to 750 litres of milk are taken for the same weight. The theory of cheese formation is not well known, but it appears that fermentation plays an important part in it. W. Hallier has proved that freshly made cheese is filled with ferment nuclei (*Kernhefe*).

Cheese cannot be formed without this ferment, and by the addition of suitable ferments the duration of the cheese-ripening process and the quality of the cheese may be to some extent regulated at will. By exposure to air cheese undergoes changes which may be best observed in skimmed-milk cheese. When new or young its colour is white. By being kept so that it does not dry, it turns yellow and often becomes transparent, waxy, and then exhibits the peculiar odour of cheese. When cheese gets very old it becomes a soft pasty mass, this change commencing at the outside and progressing towards the interior. The waxiness of cheese is due either to an evolution of ammonia or of acid. Mild cheese usually exhibits an acid reaction, while strong cheese is ammoniacal. Chemically speaking, skimmed-milk cheese is a compound of caseine with ammonia or ammonia bases, amylamine for instance. The so-called dry cheeses, green Swiss cheese, consists of an infusion of herbs, *Melilotus*, &c., with volatile fatty acids, valerianic, capric, caproic acids, and indifferent substances, leucin, &c. The composition of sweet milk cheese (*a*) and of sour skim-milk cheese (*b*) is exhibited by the following table:—

	a.	*b.*
Water	36·0	44·0
Caseine	29·0	45·0
Fatty matter...	30·5	6·0
Ash	4·5	5·0
	100·0	100·0

The results of the researches of Payen on cheese are quoted below in 100 parts for the following kinds:—1. Brie. 2. Camembert. 3. Roquefort. 4. Double cream cheese. 5. Old Neufchatel cheese. 6. New Neufchatel cheese. 7. Cheshire. 8. Gruyère. 9. Ordinary Dutch. 10. Parmesan cheese.

			I.		
	1.	2.	3.	4.	5.
Water	45·20	51·90	34·50	9·50	34·50
Nitrogenous matter ...	18·50	18·90	26·50	18·40	13·00
Nitrogen	2·93	3·00	4·21	2·92	3·31
Fatty matters	25·70	21·00	30·10	59·90	41·90
Salts	5·60	4·70	5·00	6·50	3·60
Non-nitrogenous organic matter and loss	5·00	4·50	3·90	5·70	7·00

			II.		
	6.	7.	8.	9.	10.
Water	36·60	35·90	40·00	36·10	27·60
Nitrogenous matter ...	8·00	20·00	31·50	29·40	44·10
Nitrogen	1·27	4·13	5·00	4·80	7·00
Fatty matters	40·70	26·30	24·00	27·50	16·00
Salts	0·50	4·20	3·00	0·90	5·70
Non-nitrogenous organic matter and loss	14·20	7·60	1·50	6·10	6·60

The varieties mentioned under I. exhibit an alkaline reaction, and contain with ammonia cryptogamic plants, or, as it is termed, are mouldy. The varieties under II., so-called boiled, strongly pressed and salted, cheese, exhibit an acid reaction, as also does freshly prepared caseine. A portion of the fat contained in the cheese is even from the first decomposed into glycerine and fatty acids.

Emmenthaler (*a*) and Backstein (*b*) cheese are composed, according to Lindt's researches (1868), as follows:—

	a.		*b.*	
Water	37·4	36·7	45·2	35·8
Fatty matters	30·6	30·5	28·2	37·4
Caseine	28·5	29·0	23·2	24·4
Salts	3·5	3·8	3·4	2·4
	100·0	100·0	100·0	100·0

The results of E. Hornig's recent analyses (1869) of different kinds of cheese are:—

	1.	2.	3.	4.	5.	6.	7.	8.
Water	38·66	56·60	51·21	57·64	36·72	34·08	59·28	49·34
Fatty matters ...	20·14	17·05	9·16	20·31	33·69	28·04	10·44	20·63
Caseine	34·90	18·76	33·60	18·51	25·67	23·28	24·09	24·26
Salts...	6·17	6·78	6·01	3·51	3·71	5·58	6·17	5·45
Loss...	0·13	0·81	0·02	0·04	0·21	0·02	0·02	0·32
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

1. Dutch cheese. 2 and 3. Ramadoux cheese, made in Bavaria. 4. Neufchatel cheese. 5. Gorgonzola cheese. 6. Bringen or Liptau cheese, from the Zyps Comitat, Hungary. 7. Schwarzenberg cheese. 8. Limburg cheese, made in the environs of Dolhain-Limburg, in Belgium.

Freshly made caseine mixed with lime is used as a kind of cement. Caseine is also used in calico-printing as a mordant; and a solution of caseine in borax is used instead of glue. In the seeds of the leguminous plants, peas, beans, lentils, &c., is met with a nitrogenous substance which is soluble in water and precipitable therefrom by weak acids; this material is very similar to caseine, and according to M. J. Itiers's accounts, peas and beans are in China boiled with water and strained, and to the liquid thus obtained some solution of gypsum is added, whereby the vegetable caseine (legumine) is coagulated, and the coagulum thus obtained is treated as that of milk, obtained by the addition of rennet to the latter. The mass so obtained gradually becomes like cheese in all respects.

MEAT.

Generalities. That which we term butchers' meat is the muscular substance of slaughtered animals, together with more or less fat and bone, so that the meat exhibited for sale contains on an average in 100 parts:—

Muscular tissue	16
Fat and cellular tissue	3
Bones	10
Juices	71
	100

Muscular tissue is histologically composed of a variety of complex tissues and fluids, the basis of which is animal fibre or fibrin, an organised proteine compound. The muscular fibre held together by cellular tissue forms the muscles, fat being deposited in the cellular tissue and in cells peculiarly constructed for that purpose. Blood-vessels, lymph-vessels, nerves, and other organised tissues are dispersed through the muscles and serve a variety of physiological purposes. The muscular tissue is impregnated with a proteine fluid in which are met with a variety of other substances, as kreatinin, hypoxanthin, kreatin, inosite or muscular sugar, lactic acid, inosinic acid, extractive matter, and inorganic salts—among these chloride of potassium and phosphate of magnesia.

Constituents of Meat. The average result of a great number of researches recently made on the large scale concerning the quantity of water contained in the meat of fattened, and half- or non-fattened animals, are the following:—

	Lamb.	Sheep.	Bullock.	Pig.
In the non-fattened meat	62	58	—	56
,, ,, half-fattened meat	—	50	54	—
,, ,, fully-fattened meat	49	40	46	39
,, ,, fat meat	—	33	—	—

It hence appears that with an increase of fat the quantity of water present in meat decreases, a portion being replaced by fat. Well fed and fattened meat contains for equal weights about 40 per cent more dry animal matter than non-fattened meat while in highly fattened meat it may amount to 60 per cent.

The difference in nutritive value of the meat of well-fattened bullocks as compared with that of non-fattened is exhibited in the following percentage results obtained by Breunlin:—

	Fattened.	Non-fattened.
Water	38·97	59·68
Ash	1·51	1·44
Fat...	23·87	8·07
Muscle	36·65	30·81
	100·00	100·00

1000 grms. contain:—

	Muscular Meat.	Fat.	Ash.	Water.
Meat from fattened bullocks	356	239	15	390
Meat from non-fattened bullocks...	308	81	14	597
Difference	+48	+158	+1	−207

Consequently the meat of fattened bullocks contains in 1000 parts 207 more of solid nutritive matter than the meat of the same in unfattened condition.

The Cooking of Meat. Meat is either roasted or boiled. By boiling, meat is very essentially altered in composition according to the time it is boiled and the quantity of water used to boil it in. The fluid in which meat has been boiled contains soluble alkaline phosphates, salts of lactic and inosinic acids, phosphate of magnesia, and a trace of phosphate of lime. In order to be of the highest nutritive value, meat should retain all its soluble constituents; hence boiled meat loses much in nutritive power. The albumen contained in meat is lost by boiling according to the usual plan. Meat intended to be boiled should be immersed in boiling water to which some salt has been added, the meat being put in while the water boils violently, whereby so great a heat is at once imparted to the outer portions of the meat as to coagulate the albumen, which then acts as an impermeable layer, retaining the juices in the meat. Liebig's directions for making good broth are the following:—Lean meat is minced, mixed with distilled water, to which a few drops of hydrochloric acid and common salt are added. After having been digested in the cold for about an hour, the liquid is strained through a sieve, and upon the residue some distilled water is again poured so as to extract all soluble matter. In this way an excellent and highly nutritive cold solution of extract of meat is obtained; this may be drunk without being heated, and contains albumen in solution, which is coagulated by heating. 100 parts of beef yield an extract containing 2·95 parts of albumen and 3·05 parts of other constituents of meat not coagulable by heat. Chevreul obtained from 500 grms. of beef containing 77 per cent water, 27·25 grms. of extract, in which were 3·25 grms. fat; deducting these there remain 4·8 per cent extract. The bulk of this fluid extract was 1·25 litre, the weight 1013 grms., and it contained:—

Water		991·30
Organic matter	Soluble in alcohol	9·44
	Insoluble in alcohol	3·12
Alkaline salts		8·67
Earthy phosphates...		0·46
		1013·09

Broth made from beef contains only 3 parts of meat substance inclusive of glue and fat.

Under the best conditions, 1 kilo. of beef yields:—

Soluble in cold water	60	Coagulated albumen	29·5
		Albumen in solution	30·5
Insoluble in cold water	170	Glue-yielding substance	6·9
		Fibrous matter	164·0
Fat	20		
Water	750		

The Boiling of Meat. We have already stated that the meat intended to be boiled should be immersed in boiling water and the fluid kept boiling for a few minutes, so much cold water being next added as will reduce the temperature of the liquid to 70° or 74°. At that heat the liquid should be kept for some hours to produce a very savoury, sweet, succulent piece of boiled meat. If, however, it is desired to make a strong broth, lean meat is first minced, next well exhausted with cold water, and then slowly heated—best on a water-bath—and just allowed to come to the boil over a slow fire. The liquid is strained from the solid meat, and the latter put into a clean cloth and well pressed. The residue is fit only for the making of manure. The broth may be coloured with caramel if desired. Broth so made contains all the soluble constituents of meat, and exhibits an acid reaction owing to the free lactic and inosinic acids. Broth does not owe its good properties to the gelatine it contains, this substance being present in very small quantities, while the so-called *bouillon tablettes* obtained from bones are altogether unfit for food. These tablettes should not be confused with solid meat-extract cakes of Russian make, which contain, according to Reichardt (1869):—

Water driven off at 100°	15·13 per cent.
Ash	4·75 ,, ,,
Fat	0·22 ,, ,,
Nitrogen	10·57 ,, ,,
Substance soluble in alcohol at 80 per cent	38·09 ,, ,,

When broth is boiled for a long time it becomes deep coloured and assumes the very agreeable flavour of roast meat. Evaporated upon a water-bath it yields a pasty deep brown-coloured mass, 18·27 grms. of which yield, with 1 lb. of hot water and the addition of some salt, a very strong and excellent soup. 32 lbs. of bones with the adhering scraps of lean meat yield 1 lb. of this extract. Extract of meat as generally met with is now made in South America by several firms, viz., at Fray-Bentos, Uruguay, Gualeguaychu (Entre Rios). 1 kilo. of this extract contains all the soluble portion of 34 kilos. of meat without bones, or 45 kilos. of average butchers' meat. Australian extract of beef (the American extract is of mutton and beef mixed, manufactured by R. Tooth) is largely imported into Europe. The chief test for the purity of the extract of meat is its solubility in alcohol at 80 per cent, next the quantity of moisture it contains, and the absence of albumen and fat. 60 per cent of the extract at least should be soluble in alcohol. The quantity of water amounts to about 16 per cent, the nitrogen to 10 per cent, and the ash to 18 to 22 per cent, consisting essentially of phosphate of lime and magnesia, chlorides of the alkalies, among which potassium chloride predominates.

Preservation of Meat. Among the many methods employed for the preservation of meat, that by complete exclusion of air ranks foremost. Appert's plan of packing meat in tin canisters, from which the air is completely exhausted, is generally the following:—The meat, or very concentrated soups, game, &c., is put into tin canisters, which are thoroughly filled. A lid is then soldered on, in which a small hole is made for the purpose of entirely filling any interstices with gravy. This having been done, the small hole is soldered over, after which the canisters are placed in a cauldron filled with brine and boiled therein for a half to four hours, according to the size of the canisters. When any of them is not well soldered, there will issue from the leakage smaller or larger vesicles of air and vapour, and where such is the case hot solder is applied to the spot. By this boiling the albuminous substances are coagulated and converted into a less-readily putrescible modification. The oxygen of the air contained in the canisters is partly converted into carbonic acid, partly deozonised, and thus rendered ineffective for the production of putrescence. After having been submitted to the action of boiling heat for some time, the canisters are placed in a room heated to 30°, and left there in order to test whether putrefaction can set in, manifested by the bulging outward of the top cover, which, if the operation has been thoroughly successful, is usually somewhat concave in consequence of a vacuum having been formed inside the tin. After having been thus tested for several days, the canisters may be considered sound, and will keep for an indefinite period. Dr. Redwood's method of preserving meat under a layer of paraffin, and Shaler's plan of preserving meat in dry carbonic acid gas at 0°, are in principle the same as Appert's method.

Preservation of Meat by Withdrawal of Water. Meat may be preserved by drying it or salting it, both methods being based upon the withdrawing of the water. Although drying is the best method of preserving meat, it is an operation attended with very great difficulty. The natives of North and South America cure meat by cutting it into thin strips, removing the fat, and rubbing Indian-corn meal on the surface. Thus prepared, the meat is exposed to the heat of the sun and dries rapidly, forming a flexible non-putrescent mass, which in North America is termed *Pemmikan*, in South America *Tassajo*, and in South Africa *Biltongue*. 100 parts of beef, which is, after drying, rolled up so as to form a compact mass, yield 26 parts of tassajo. The drying of meat is in Europe never effected on a large scale, partly on account of the low temperature, partly on account of the necessity of cutting the meat into pieces, rendering it in many instances unfit for culinary purposes.

Many preparations of flour and meat extract have been introduced at different times under the name of meat-biscuit, first made in 1850 by Gail Bordon, at Galveston, in Texas, U.S., and greatly improved upon by C. Thiel, at Darmstadt. The latter minces fresh lean meat, next exhausts it with water, and uses the liquid obtained for mixing with the flour instead of water. The large biscuit manufacturing firms in England, especially Huntley and Palmer at Reading, prepare patent meat-biscuits or wafers, made with Liebig's extract of meat and Hassall's flour of meat. On the Continent, E. Jacobsen, at Berlin, prepares a similar biscuit, more especially with the view of preparing soup. To the mixtures of animal and vegetable matter prepared so as to be suitable for keeping for a length of time belong the pea-sausages, first made by Grüneberg in Berlin, and largely used during the late war as an excellent food for the German armies.

Salting Meat. This method of preserving meat, based upon the principle of withdrawing water, has been used from time immemorial. The salt, while penetrating into the meat and thereby hardening it, displaces the water and aids the preservation of the substance. The freshly-slaughtered meat is first rubbed with coarse salt, and then left in a cask with salt for some days. It is next pressed and put into another cask, the wood of which has been previously soaked with brine. Some salt is then added, and lastly the brine, which had been obtained by pressing the meat, is poured over it, and the lid of the cask put on. Frequently some nitrate of potash and sugar are added, as well on account of the antiseptic property of these substances as for imparting a bright red colour to the meat.

Salt, however, not only withdraws water from the meat, but also, as has been proved by Dr. Liebig's researches, some of the very best and essential portion of the juices of the meat, including albumen, lactic and phosphoric acids, magnesia, potash, kreatin, and kreatinin. Hence it is clear, that unless these substances are in some way or other added to the salted meat, its use as food for a lengthened period cannot fail to become injurious to the system, and it is surmised that scurvy is due to this condition of salt meat. Liebig has suggested that meat, instead of being treated with dry salt, should be salted with a strong brine made up of common salt, Chili saltpetre, chloride of potassium, and extract of meat. The salt to be used for making this brine should be previously purified by the application of a solution of phosphate of soda, whereby lime and magnesia are precipitated. Cirio's method of meat preservation, which was exhibited in 1867 at the Paris Exhibition, consists in placing the meat *in vacuo* and then forcing brine into it. By this process the nutritive value of meat is much impaired owing to the loss of the juices.

Smoking or Curing Meat. The *rationale* of this process and the preservative action of the smoke have not been scientifically elucidated. In the first place the heat of the smoke dries the meat, while, further, smoke contains a creosote, which, according to the more recent researches of Hlasiwetz, Gorup-Besanez, Marasse, and others, essentially consists of a mixture of $C_7H_8O_2$, $C_8H_{10}O_2$, and $C_9H_{12}O_2$. This creosote possesses the property of coagulating the albuminous substances of meat, and once coagulated and thereby rendered insoluble these substances are not capable of decay, or only so after a very great lapse of time. Smoke, moreover, contains some pyroligneous acid and other creosote-like substances (oxyphenic and carbolic acids), which undoubtedly play some part in the preservative action.

Vinegar is an excellent preservative of meat, especially in hot summer weather. Abroad meat is frequently put into a clean linen cloth which is thoroughly soaked with vinegar, some salt also being sprinkled on the cloth. Meat kept for a few days in this manner is very tender and readily digested. It is very probable that vinegar might be advantageously employed on the large scale for the preservation of meat together with complete exclusion of air. In order to prevent the vinegar extracting the juices of the meat, the latter should be exposed to the action of the vapours of strong vinegar.

Lamy more recently, and Braconnot, Robert, and De Dombasle, nearly half a century ago, proposed to preserve meat by the aid of sulphurous acid gas, pieces of meat weighing some 2 to 3 kilos. being exposed to the action of this gas for ten minutes, while larger pieces of 10 kilos. and more, are exposed to the action of the gas for 20 to 25 minutes. After having been exposed to fresh air for some minutes for the purpose of getting rid of the excess of the gas, the meat is coated with a brush with a solution of albumen in a decoction of marsh-mallow root, to which some molasses have been added. Very recently meat has been preserved by first drying it in a current of hot air and next coating it with a film of caoutchouc or gutta-percha, by immersing the meat in a solution of these substances in chloroform or sulphide of carbon. It is very generally known that a temperature below freezing-point is a most perfect protection against decay of animal matter; hence ice is largely used for the preservation of fish in summer time. Meat as well as game and poultry are best preserved in hot weather in ice pits. In no country of the world is so much use made of this mode of preserving meat and vegetables as in Russia, where the very severe winter is turned to good account by the preserving of all kinds of animal food; in fact, oxen, sheep, hogs, deer, and all kinds of game and poultry are brought to market in a frozen condition, and may be kept so for any length of time without impairing the goodness or taste after cooking. At St. Petersburg large stores of frozen animal food and game brought from distances of hundred of miles are kept throughout the winter. At the Dornburg, near Hadamar (Province of Nassau, Prussia), a natural permanent ice store exists wherein perishable food is kept stored in large quantity. The artificial production of ice by means of Carré's machine is employed in New South Wales for the freezing of meat, which is next packed in ice ready for transport.

DIVISION VI.

DYEING AND CALICO PRINTING.

On Dyeing and Printing in General.

Dyeing and Printing in General. The object of the art of dyeing is to impart to textile fibres, chiefly in the shape of woven tissue, but in many instances as yarn, some colour or other. Dyeing is distinguished from painting by the fact that the pigments are fixed to the animal and vegetable textile fibres according to certain physico-chemical principles, and are not, as in painting, simply fixed by adhesion to the surface, although painters and artists occasionally use the same pigments. Printing consists in the duplication of coloured patterns, and is a very important part of dyeing.

Dyes. The materials employed for the production of colours, the dyes and pigments, are partly of mineral, animal, and vegetable origin, partly artificially obtained—that is, the products of modern chemistry. Among the very large number of inorganic pigments few only are as such fit for use, and if employed at all it is by an indirect or circuitous process, that is, they are produced upon the woven fabric itself. For instance, chromate of lead is obtained by first impregnating the woven tissue with acetate of lead, after which the fabric is treated with a solution of bichromate or neutral chromate of potash, the result being the formation of a solid adhering chromate of lead. Among many other inorganic pigments may be enumerated—Berlin blue; hydrated oxide of iron, for drab, nankeen, or rust colour; bistre colour, hydrated oxide of manganese: chrome-green, oxide of chromium. Among the dyes of animal origin are—The ancient Tyrian purple, derived from a mollusc, a native of the Mediterranean, now not used; kermes (*Coccus ilicis*); cochineal (*Coccus cacti*); lac dye (*Coccus laccæ*). A much larger number of dyes are obtained from the vegetable kingdom. It appears from recent researches, that a large number of the so-called vegetable pigments are present in the plants themselves in a colourless condition, becoming coloured by the action of the atmosphere. It is impossible to mention any general properties of the vegetable pigments, because excepting the fact that they are all coloured, they are not possessed of any property common to all. Nearly all dyes fade by the combined action of sunlight and moist air. Chlorine destroys most colours; while many dyes are bleached, not destroyed, by sulphurous acid. We owe to the researches of modern chemistry a class of pigments which surpass in beauty almost all the native dye materials. These chemically prepared dye materials are chiefly derived from coal-tar, more particularly from benzol, toluol, carbolic acid, anthracen, and naphthalin. The pigments derived from these substances are commonly termed aniline or coal-tar colours, fuchsin, magenta, aniline blue and violet, Manchester yellow, aniline orange, picric acid, aniline brown, coralline, alizarine (artificially prepared from anthracen), magdala red, aniline black, and aniline green. Among the chemically prepared colouring matters should be mentioned those obtained by the decomposition of the alkaloids (cinchonine, quinine, &c.), chinoline blue, quinine green (thalleiochine), and also murexide, a product of the decomposition of uric acid.

Lake Pigments. The so-called lakes are compounds of starch, alumina, oxide of tin, oxide of lead with sometimes carbonate of lime, baryta, or oxide of antimony, with the colouring matter of madder, cochineal, woad, logwood, tar-colours (viz. coralline, fuchsin, aniline violet), but as yet these substances are not prepared in definite proportions. By paints we understand substances which as a rule are insoluble in water and are mixed with either weak glue solution, being then termed water-colours, or with linseed oil, called oil-paints. To these pigments belong white-lead, red-lead, ultramarine, Berlin blue, vermillion, chrome-yellow, bone-black, &c. The ordinary water-colours are insoluble in water, being finely suspended therein by the aid of gum, white of egg, gum tragacanth, &c. The pastel pigments used for drawing are made up of various pigments, mixed with pipe-clay, soap, and some tragacanth mucilage, and moulded into cylindrical sticks.

Colouring Materials. *Dyeing* means strictly the tinging or colouring of absorbent substances by impregnating them with solutions of colouring matters. It is thus opposed to painting, which consists in laying a colour upon the surface to be coloured. In the art of dyeing some colouring matters are applied by immersing the tissue to be coloured in the decoction or solution of the pigment. Some substances are applied to the surface of the woven fabric by the intervention of what is technically termed a mordant, which is in the case now under consideration only a means of obtaining adhesion, as when, for instance, ultramarine is fixed by the aid of white of egg. Sap-colours are substances more or less soluble in water, covering very slightly, and more or less translucent, as sap-green, gamboge, carmine solution, many of the tar-colours, &c.

The Coal-Tar Colours.

Coal-Tar. This substance is very largely obtained as a by-product of the dry distillation of coal for the purpose of gas manufacture, and is a most complex mixture of a very large number of substances, among which are fluid and solid hydrocarbons (benzol, toluol, cumol, cymol, anthracen, naphthalin); acids (carbolic or phenylic, cresylic, phlorylic, rosolic); bases (aniline, chinoline, odorine, picoline, toluidine, coridine, &c.), and asphalte-forming materials. Leaving the small quantity of basic substances out of the question, 100 parts of tar consists of the following substances:—

Benzol	1·5
Naphtha	35·0
Naphthalin	22·0
Anthracen	1·0
Carbolic acid	9·0
Pitch	31·5
	100·0

By fractional distillation of tar we obtain, on the one hand, light oils, from which benzol and its homologues are separated; on the other hand, heavy tar oil, which is used for making carbolic acid; while, lastly, anthracen is separated from the pitch.

Approximatively, the following table shows the quantity of the various materials obtained by the dry distillation of coal:—

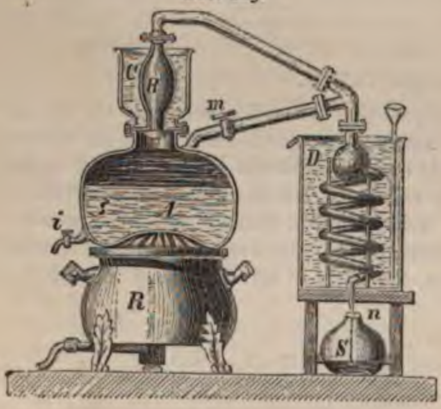
100 kilos. of coal yield	3·00 kilos. of tar.
100 kilos. of tar yield	0·75 to 1 kilo. of anthracen.
„ „ „	3·00 kilos. of crude benzol.
„ „ „	1·50 kilos. of pure benzol.
„ „ „	3·00 kilos. of nitro-benzol.
„ „ „	2·25 kilos. of crude aniline.
„ „ „	3·37 kilos. of crude aniline red.
„ „ „	1·12 kilos. of pure fuchsin.

For the preparation of 1 kilo. of pure fuchsin 60 cwts. of coal are required.

Benzol. Chemically speaking, benzol or benzine is a fluid hydrocarbon, 6_6H_6, discovered in 1825 by Faraday among the products of the dry distillation of oil, in the liquid resulting from the strongly compressed oil gas. In 1833 Mitscherlich obtained this body by distilling benzoate of lime. Leigh, at Manchester, 1842, first discovered benzol in coal-tar; and to Mansfield's researches is due the method of separating benzol from tar by a process available on the large scale.

The benzol as met with in commerce is a mixture of benzol boiling at 80·4° with toluol, C_7H_8, boiling at 108°; xylol, C_8H_{10}, boiling at 130°; cumol, C_9H_{10}, boiling at 151°; and cymol, $C_{10}H_{12}$, boiling at 175°; benzol and toluol, however, predominate. Abroad benzol is sold to the aniline makers at a certain specified percentage of benzol, C_6H_6; for instance, benzol at 30 to 40 per cent contains by bulk or weight, as may be agreed upon, the above percentage of the compound C_6H_6, the rest being 60 to 70 per cent of toluol and xylol, forming a fluid which is suitable for making aniline red, while for aniline blue or black a fluid at 90 per cent benzol, C_6H_6, is required. The boiling-point of the benzols usually employed for making the so-called tar-colours varies from 80° to 120°, while the specific gravity varies from 0·85 to 0·89.

FIG. 265.



Benzol is prepared from light tar oil which boils below 150°. The apparatus invented by Mansfield for this purpose is shown in Fig. 265. A is the still placed on a furnace, R; C is filled with cold water. As soon as the oil in the still begins to boil, the vapours are condensed in B and flow back into A; this continues until the water in C has been heated to a certain temperature, when the vapours are condensed in the cooler, D, the liquid flowing at *n* into the carboy, S. As soon as the water in C begins to boil, all the substances contained in the tar-oil and volatile at 100° are condensed and collected in S. A very pure benzol is prepared with this apparatus. By opening the tap *m*, the hydrocarbons which boil above 100° can be rectified. The stopcock, *i*, is used for emptying the still. In the benzol works the apparatus exhibited in Fig. 266 is used. A is the still, B the condenser, C a water tank. At the commencement of the operation the water in C is heated by means of the steam-pipe D, which communicates with the steam boiler. The tube G is attached to the still; *i* is a contrivance for filling, *b* for emptying it. The condensed water is

FIG. 266.

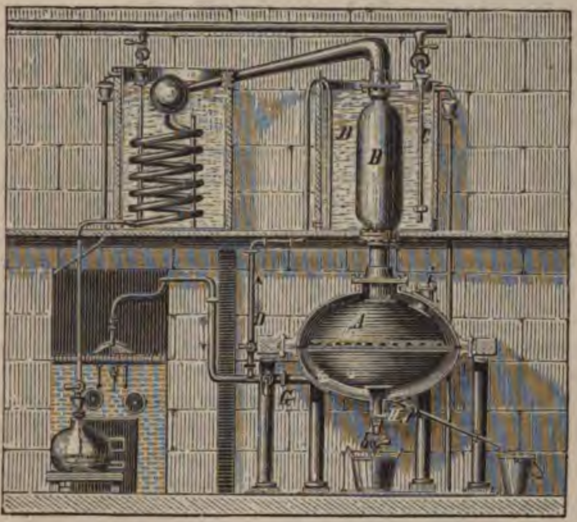
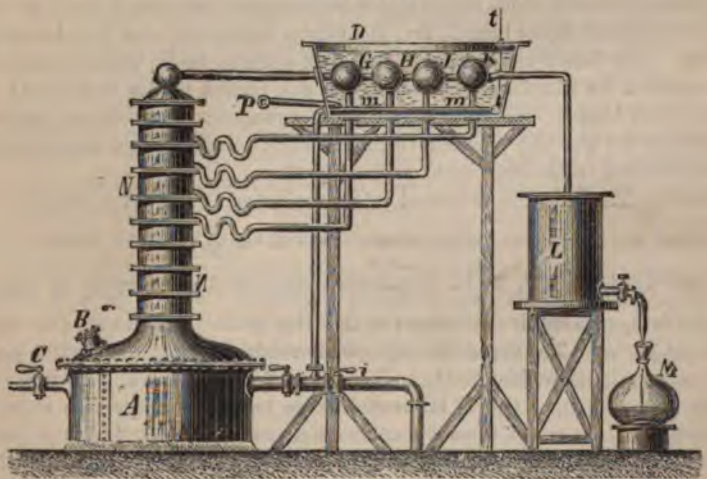


FIG 267.



carried off by means of H. By freezing benzol and pressing the solid substance obtained it may be rendered quite pure.

In the year 1860, Dr. E. Kopp, at Turin, showed that the preparation of benzol might be advantageously effected by the use of an apparatus similar in construction to that employed in spirit distilleries. Coupier has constructed an apparatus upon this principle, which is shown in Fig. 267. A is the still; at B the crude benzol is poured in; C is a steam-pipe for heating the still and its contents. The vapours evolved from the boiling liquid are carried into the column N, which acts as a dephlegmator, by which a first fractionation is effected. The volatile vapours which are not condensed in N are carried to the apparatus D, which is filled with a solution of chloride of calcium. This apparatus is kept at a uniform temperature determined by the thermometer, *t*, and maintained by the steam-pipe *m*.

The steam conveyed by the heating pipe escapes by P. When it is desired to prepare pure benzol the chloride of calcium solution is heated to 80°. The vapours which are conveyed to G are a mixture of benzol, toluol, &c. As the temperature of the receiver G does not exceed 80°, the vapours of toluol and other homologous compounds, as xylol, are condensed; while the vapours still uncondensed are carried to the receivers H, I, and K, losing or depositing there the last traces of the less volatile hydrocarbons, becoming finally condensed in L, surrounded with cold water, and trickling down into the carboy, M. The fluid condensed in G, H, I, and K, flows back into the column N. As the receiver G contains the heaviest oils these are carried, for the purpose of dephlegmation, to the lower portion of the column, while the products condensed in K are conveyed by pipes into the upper portion of the column. When it is desired to prepare toluol instead of benzol the chloride of calcium apparatus is heated to 108° to 109°.

H. Caro, A. and K. Clemm, and F. Engelhorn have suggested, instead of making benzol from coal-tar, it should be extracted from coal-gas by causing this to be passed slowly through tar-oils which have a higher boiling-point than benzol, toluol, &c., and to extract by distillation the benzol, &c., from these heavy oils after they have become saturated. The heavy oils can serve the same purpose again, while as regards the depreciation of the illuminating power of the gas caused by the withdrawal of the hydrocarbons, benzol, &c., present in the gas as vapours, the authors suggest the saturation of the gas with petroleum oil (benzoline). This mode of making benzol is not yet practised on the large scale.

Nitro-benzol. The benzol is converted into nitro-benzol by the aid of nitric acid; the commercial article is a mixture of nitro-benzol, $C_6\left\{\begin{matrix}H_5\\NO_2\end{matrix}\right.$, nitro-toluol, $C_7\left\{\begin{matrix}H_7\\NO_2\end{matrix}\right.$, and nitro-xylol, $C_8\left\{\begin{matrix}H_2\\NO_2\end{matrix}\right.$. E. Mitscherlich discovered nitro-benzol in 1834, and C. Collas first prepared this substance on the large scale at Paris under the name of *Essence de Mirbane*. The apparatus employed formerly for the making of this preparation was contrived by Mansfield, and consists of a convoluted glass tube, which towards its top or upper end is bifurcated so as to form two separate tubes fitted with funnels. Into one of these a continuous stream of benzol, and into the other strong nitric acid, is caused to flow; and while these liquids are carried downwards by gravitation through the windings of the tube the combination takes place, and the warm liquid is so far cooled that it can be collected at the lower end of the tube. The crude nitro-benzol thus obtained is rendered pure by first washing it with water and next with a dilute solution of carbonate of soda.

Para-nitro-benzoic acid, a substance isometric with nitro-benzoic acid, is found in the washings of the nitro-benzol.

It is preferable, however, to prepare nitro-benzol from a mixture of 2 parts of nitric acid at 40° Beaumé (sp. gr. 1·384) and 1 part of concentrated sulphuric acid, the operation being carried on in closed vessels very similar to those in use for making aniline. The upper part of the apparatus is fitted with a tube for conveying the nitrous acid fumes to a chimney, while an S-shaped tube connects the apparatus with the tank containing the acid mixture. The quantity of benzol intended to be nitrated is introduced into the apparatus at one time; the mixed acids are gradually poured into the benzol, and the reaction aided by a stirring apparatus. Any benzol volatilised by the heat generated by the reaction is condensed by an apparatus fitted to the reaction vessel and is thus saved. The end of the reaction is indicated by the liquid becoming colourless and being separated into two distinct strata by the addition of water. The acid is first diluted to 50° B. (sp. gr. 1·532) and the fluids are separated by decantation. The nitro-benzol is purified by washing with water, the dilute acid mixture being used either in the making of sulphuric acid or in other chemical processes, such as the preparation of superphosphates. On E. Kopp's suggestion nitro-benzol is now made by the aid of a mixture of nitrate of soda and sulphuric acid. 100 kilos. of benzol yield 135 to 140 of nitro-benzol.

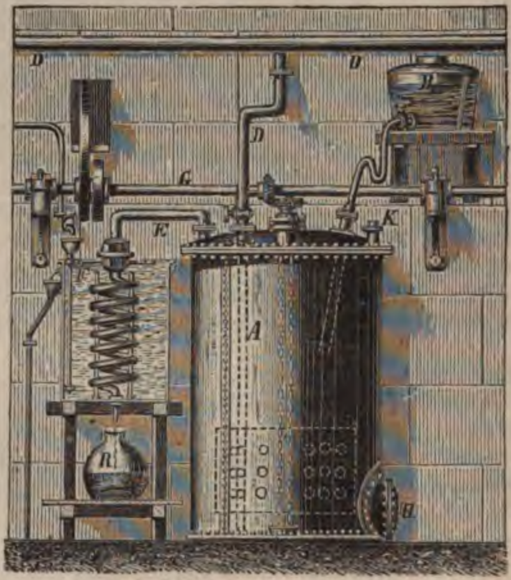
We distinguish three different kinds of nitro-benzol, viz.:—1. Light nitro-benzol, boiling between 205° and 210°. This is used in perfumery and soap-making in very large quantities under the name of artificial oil of bitter almonds, or *Essence de Mirbane*, sp. gr. = 1·20 (= 24° B.) 2. Heavy nitro-benzol, boiling between 210° and 220°, possessing a peculiar fatty smell. It is not used in perfumery, but chiefly for the preparation of aniline red; sp. gr. = 1·19 (= 28° B.) 3. Very heavy nitro-benzol, boiling between 222° and 235°, sp. gr. = 1·167 (= 58° B.) Of disagreeable odour, this kind is chiefly used for the preparation of aniline intended for making aniline blue.

Aniline. The crude aniline used for the preparation of the so-called tar or aniline colours is essentially a mixture of aniline, C_6H_7N, toluidine, C_7H_9N, and the pseudo-toluidine discovered by Rosenstiehl, a body isomeric with toluidine. This kind of aniline is known in the trade as aniline oil. Pure aniline and pure toluidine only yield pigments under special conditions. Aniline was discovered at Dahme, in Saxony, by Dr. Unverdorben, in 1826, among the products of the dry distillation of indigo, and in 1833 Runge, at Oranienburg, near Berlin, discovered its presence in coal-tar. Runge also discovered that aniline yielded, when brought into contact with a solution of hypochlorite of lime (bleaching-powder), a beautiful violet colour; hence the name kyanol (*blue colouring oil*). Dr. von Fritzsche, St. Petersburg, 1841, thoroughly investigated the substance obtained by Dr. Unverdorben from indigo, ascertained its composition, and called it aniline, from *anil*, the Portuguese term for indigo. In the year 1842 Zinin found that when nitro-benzol was treated with sulphuretted hydrogen, there was formed a base which he termed benzidam. The further researches of O. L. Erdmann and Dr. A. W. Hofmann, brought the fact to light that Dr. Unverdorben's crystalline, kyanol, benzidam, and aniline were the same substance, to which the name aniline was then finally given. We owe to the extensive researches of Dr. A. W. Hofmann our present knowledge of aniline and its compounds.

Coal-tar contains 0·3 to 0·5 per cent of aniline, but its extraction from tar is attended with so many difficulties that it is preferred to prepare aniline from nitro-benzol by a reaction discovered by Zinin; that is to say, to bring nitro-benzol into contact with reducing agents. 1 molecule of nitro-benzol, $C_6H_5N_2O = 123$, yields 1 molecule of aniline, $C_6H_7N = 93$. In practice it is assumed that 100 parts of nitro-benzol yield 100 parts of aniline.

Although sulphuretted hydrogen completely reduces nitro-benzol to aniline, the trade working on the large scale prefers to follow Béchamp's method, the treatment of nitro-benzol with iron-filings and acetic acid. The apparatus in use for carrying out this operation was devised by Nicholson, and is exhibited in Fig. 268. It consists essentially of a cast-iron cylinder, A, of 10 hectolitres (220 gallons) cubic capacity. A stout iron tube is fitted to this vessel reaching nearly to the bottom of the cylinder. The upper part of this tube is connected with the machinery G, while the surface of the tube is fitted with steel projections. The tube serves to admit steam as well as acting as a stirring apparatus. Sometimes, instead of this tube, a solid iron axle is employed, and in this case there is a separate steam-pipe, D. Through the opening at K the materials for making aniline are put into the apparatus, while the volatile products are carried off through E. H serves for emptying and cleaning the apparatus. The S-shaped tube connected with the vessel B acts as a safety-valve. When it is intended to work with this apparatus, there is first poured into it through K 10 kilos. of acetic acid at 8° B. (= sp. gr. 1·060), previously diluted with six times the weight of water; next there are added 30 kilos. of iron-filings or cast-iron borings, and 125 kilos. of nitro-benzol, and immediately after the stirring apparatus is set in motion. The reaction ensues directly, and is attended by a considerable evolution of heat and of vapours. Gradually more iron

FIG. 268.



is added until the quantity amounts to 180 kilos. The escaping vapours are condensed in F, and the liquid collected in R is from time to time poured back into the cylinder, A. The reduction is finished after a few hours. The resulting thick magma exhibits a reddish-brown colour, and consists essentially of hydrated oxide of iron, aniline, acetate of aniline, acetate of iron, and excess of iron. Leaving the acetic acid out of the question, the process may be elucidated by the following formula:—

$$\underbrace{C_6H_5NO_2}_{\text{Nitro-benzol.}}+H_2O+Fe_2=\underbrace{C_6H_7N}_{\text{Aniline.}}+\underbrace{Fe_2O_3}_{\text{Peroxide of iron.}}$$

This magma is either first mixed with lime or is put into cast-iron cylinders shaped like gas-retorts, and submitted to distillation, the source of heat being either an open fire or steam. The product of this operation, consisting of aceton, acetaniline, aniline, nitro-benzol, &c., is rectified by a second distillation, care being taken to collect only the product which comes over between 115° and 190°; but a product which comes over at between 210° and 220° is very suitable for the preparation of aniline blue. The aniline oil thus obtained is a somewhat brown-coloured liquid, heavier than water, and pure enough for the preparation of the aniline colours. According to Brimmeyer, acetic acid is not necessary, and a very good result may be obtained by mixing nitro-benzol with 60 parts of pulverised iron with acidified water (2 to 2·5 per cent of hydrochloric acid upon the weight of nitro-benzol), and leaving this mixture to stand in a retort for some three days before distilling off the aniline oil. In the aniline-oil works of Coblentz Frères, at Paris, nitro-benzol is reduced by the aid of iron-filings, a portion of which have been coated with copper by being immersed in a solution of the sulphate.

The composition of the aniline oil—essentially a mixture of aniline, toluidine, and pseudo-toluidine—depends upon the nature of the benzol and nitro-benzol used for its preparation. The aniline oil boiling between 180° and 195° (sp. gr. = 1·014 to 1·021 = 2° to 3° B.) is prepared from nitro-benzols which boil between 210° and 220°, and the aniline it yields is chiefly used for aniline red; while for aniline blue a very heavy nitro-benzol is employed, and for aniline violet a nitro-benzol which boils at 210° to 225°. The following table exhibits the boiling-points of the substances which have been mentioned:—

Benzol	80°	Nitro-toluol	225°
Toluol	108°	Aniline	182°
Nitro-benzol	213°	Toluidine	198°

As regards the annual production of aniline oil it is now (1871) 3,500,000 lbs., of which 2,000,000 lbs. are consumed in Germany, and the remainder in Switzerland, England, and France

I. *Aniline Colours.*

Aniline Colours. The aniline oil serves for the industrial production of the so-called aniline or toluidine colours:—1. Aniline red. 2. Aniline violet. 3. Aniline blue 4. Aniline green. 5. Aniline yellow and aniline orange. 6. Aniline brown. 7. Aniline black.

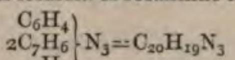
Aniline Red. 1. This pigment or dye, also known as fuchsin, azaleine, mauve, solferino, magenta, roseine, tyraline, &c., is the combination of a base, which Dr. A. W. Hofmann has named rosaniline, with an acid, usually acetic or hydrochloric. In Germany and Switzerland fuchsin is the hydrochlorate of rosaniline, $C_{20}H_{19}N_3,ClH$; while in England the acetate is used, the formula being

$$C_{20}H_{15}N_3,C_2H_4O_3.$$

The base rosaniline is a colourless substance, but its readily crystallising salts are coloured. The composition of this base is expressed by the formula, $C_{20}H_{19}N_3,H_2O$; and it is formed by the combination of 2 atoms of toluidine with 1 atom of aniline and the elimination of 4 atoms of H, which become oxidised—

$$2C_7H_9N+C_6H_7N+3O=2H_2O+C_{20}H_{19}N_3,H_2O$$

Accordingly the constitutional formula of rosaniline is:—



$$\left.\begin{array}{r}C_6H_4\\2C_7H_6\\H_3\end{array}\right\}N_3=C_{20}H_{19}N_3$$

According to Rosenstiehl's researches (1869) all the different kinds of fuchsin of commerce contain pseudo-rosaniline, a base isomeric with rosaniline.

Aniline red can be obtained from aniline oil by the application of various reagents, as, for instance:—Chloride of tin, Verguin's method; perchloride of carbon, Hofmann and Natanson's methods; pernitrate of mercury, Gerber-Keller;[*] perchloride of mercury, Schnitzer; nitric acid, Lauth and Depouilly; antimonic acid, Smith; arsenic acid, Medlock, Girard and de Laire; aniline oil, nitro-toluol, hydrochloric acid and metallic iron, Coupier. 100 parts of aniline oil yield 25 to 33 parts of crystalline fuchsin.

Notwithstanding the great danger arising from the use of arsenic acid, and the difficulty of disposing of the very poisonous residues of this mode of preparing fuchsin, the majority of the manufacturers of this dye prefer to use the arsenic acid method. According to Girard and de Laire's method 1 cwt. of aniline oil and 2 cwts. of hydrate of arsenic acid at 60° B. (=1·71 sp. gr.) are heated together for 4 to 5 hours at a temperature which should not exceed 190° to 200°. The red fused mass (fuchsin mixture or smelting) formed by this operation is broken into small lumps and then boiled with water, and as soon as the mass is dissolved it is filtered through felt or linen bags, and the filtrate poured into tanks for the purpose of obtaining crystals. After the lapse of 2 to 3 days the mother-liquor, a very poisonous liquid, which covers the crystals, is run off into perfectly water-tight tanks made of stone and coated with asphalte, and in order to precipitate the arsenic and arsenious acids there is added a mixture of washed chalk and lime, the ensuing precipitate being employed for making arsenical preparations.[†] The crystalline mass is purified by re-crystallisation. In the French fuchsin works the fused mass is dissolved in water and hydrochloric acid, and next neutralised with soda. The fuchsin is thus obtained as a crystalline cake, which is dissolved by being boiled with water, and this solution allowed to crystallise. The fuchsin thus obtained always contains arsenic and when it is desired to use a salt of rosaniline for colouring liqueurs and sweetmeats it is necessary to use a preparation made with either chloride of carbon or bichloride of mercury. The salts of rosaniline exhibit by reflected light a green golden hue; by transmitted light the colour is red. The hydrochlorate of rosaniline is usually called fuchsin, the acetate, roseine, and the nitrate, azaleine. The solutions of these salts in water or in alcohol exhibit a well-known and very magnificent carmine red. The tinctorial power is exceedingly high, since 1 kilo. of fuchsin is sufficient to dye 200 kilos. of wool. The tannate of rosaniline is very difficultly soluble in water. Fuchsin is the basis of nearly all other aniline colours; for instance, fuchsin yields violet or blue with aniline oil; fuchsin and iodide of ethyl, blue or violet. The action of the arsenic acid in the formation of rosaniline may be represented as follows:—

---

[*] The fuchsin prepared by the aid of this reagent is known as rubin, and is employed for dyeing silk and for colouring liqueurs and sweetmeats.

[†] According to Dr. Bolley, the arsenical fluids obtained can be rendered again fit for use by distillation with hydrochloric acid. On being diluted with water the arsenious acid contained in the distillate is thrown down.

$$\left.\begin{matrix}C_6H_7N\\2C_6H_9N\end{matrix}\right\} = \underbrace{C_{20}H_{25}N_3}_{\text{Aniline oil.}}+\underbrace{3As_2O_5}_{\text{Arsenic acid.}} = \underbrace{C_{20}H_{19}N_3}_{\text{Rosaniline.}}+\underbrace{3As_2O_3}_{\text{Arsenious acid.}}+\underbrace{3H_2O}_{\text{Water}}.$$

Aniline Violet. 2. This pigment, also known as aniline purple, anileine, indisine, phenanicine, harmaline, violine, rosolan, mauveine, was discovered in 1856 by Dr. W. H. Perkin, and is prepared by the action of bichromate of potash and sulphuric acid. This substance has also been prepared by other reactions, for instance, by the treatment of a salt of aniline with a solution of bleaching-powder (Bolley, Beale, Kirkham); with peroxide of manganese (Kay), and peroxide of lead (Price), both in the presence of sulphuric acid; by the action of permanganate of potash upon a salt of aniline oil (Williams); by treating aniline oil with chlorine (Smith); with ferricyanide of potassium (Smith); with chloride of copper (Caro and Dale). Industrially, only Dr. Perkin's method with the bichromate and sulphuric acid is used. The base of the violet thus obtained is mauveine, $C_{27}H_{24}N$.

The so-called *Violet Impérial* obtained by Girard and de Laire by the action of chromate of potash upon a mixture of aniline oil and hydrochlorate of rosaniline at 180°, differs from the preceding product, while another violet is obtained according to Nicholson by heating fuchsin to 200° to 215°. When a salt of rosaniline is heated with excess of aniline there are formed, before blue colours ensue, violet pigments, of which, according to Hofmann—

The red-violet is monophenyl-rosaniline.
The blue-violet is diphenyl-rosaniline.

This latter yields on being further heated triphenyl-rosaniline or aniline blue. Accordingly,—

Rosaniline red is … … … … … … … …	$C_{20}H_{21}N_3O$.
Monophenyl-rosaniline (red-violet) is … …	$C_{20}H_{20}(C_6H_5)N_3O$.
Diphenyl-rosaniline (blue-violet) is … … …	$C_{20}H_{19}(C_6H_5)_2N_3O$.
Triphenyl-rosaniline (blue) … … … … …	$C_{20}H_{18}(C_6H_5)_3N_3O$.

The violet is now named the old or *Nonpareil* violet; and we have the new or iodine violet, Hofmann's violet or dahlia colour, distinguished by the presence of the alcohol radicals, ethyl, methyl, and amyl, instead of phenyl. These new violets are obtained by heating to 100° or 110° fuchsin with alcohol as a solvent, and the iodides, or more recently, the bromides, of the alcohol radicals, the mixture being kept in closed cylindrical vessels. According to the length of time this reaction is allowed to take place there are formed:—

Monethyl-rosaniline,
Diethyl-rosaniline, or
Triethyl-rosaniline.

The most ethylised base exhibits a blue-violet colour, while the less ethylised exhibits a red hue. The methylated and ethylated violets are far more brilliant than the phenylated. The *Violet de Paris*, introduced by Poirrier and Chappat, is the product of the action of chloride of tin and similar compounds upon the methyl or ethyl aniline.

Aniline Blue. 3. This colour, also known as azuline and azurine, was first obtained in 1861 by de Laire and Girard by heating together for some hours a mixture of fuchsin and aniline oil, and treating the product of this reaction with hydrochloric acid. The blue pigment produced is known in commerce as *bleu de Paris* or *bleu de Lyons ;* in dry state it is a copper-coloured shining material, not exhibiting green or yellow by reflection, the characteristic of fuchsin and aniline violet. In order to purify the aniline blue it is dissolved in strong sulphuric acid, and this mixture heated to 150° for 1½ hours. By the addition of water to this solution the blue is precipitated in a modified and soluble form and is then called *bleu soluble.* We quote here the following methods for preparing this blue:—Rosaniline and aldehyde (Lauth); rosaniline and crude wood-spirit (E. Kopp); rosaniline and alkaline solution of shellac (Gros-Renaud and Schäffer), this is termed *bleu de Mulhouse ;* also by oxidation of methylaniline (J. Wolff); rosaniline and bromated oil of turpentine (Perkin); rosaniline and isopropyl iodide (Wanklyn); rosaniline and ethylen iodide and bromide (M. Vogel); rosaniline and iodide and bromide of aceton (Smith and Sieberg). The conversion of hydrochlorate of rosaniline (fuchsin) by heating with aniline oil into aniline blue is elucidated by the following formula:—

$$\underbrace{C_{20}H_{19}N_3,ClH}_{\text{Rosaniline salt.}}+\underbrace{3C_6H_7N}_{\text{Aniline.}} = \underbrace{C_{20}H_{16}(C_6H_5)_3N_3,HCl}_{\text{Aniline blue.}}+\underbrace{3NH_3}_{\text{Ammonia.}}.$$

The aniline blue thus prepared is rosaniline, $2\left.\begin{matrix}C_6H_4\\C_7H_6\\H_3\end{matrix}\right\}N_3$, in which 3 atoms of basic hydrogen have been substituted by 3 atoms of phenyl, C_6H_5; or, in other words, this aniline blue is triphenyl-rosaniline, the hydrochlorate of which is—$C_{38}H_{32}N_3Cl$. When a salt of rosaniline is heated with toluidine, the toluidine blue (tritolyl-rosaniline), $C_{41}H_{37}N_3 = C_{20}H_{16}(C_7H_7)_3N_3$. When aniline blue is heated, the products of the dry distillation contain diphenylamine, $C_{12}H_{11}N$, a white crystalline compound, which when moistened with nitric acid yields a magnificent blue colour. Diphenylamine and its homologue phenyl-tolylamin, $C_{13}H_{13}N$, which yields by dry distillation bleuine, $C_{39}H_{33}N_3$, are employed for the preparation of blue pigments. Dr. A. W. Hofmann found that when rosaniline is heated for a considerable length of time with iodide of ethyl or iodide of amyl, the result is that the most ethylated or amylated product (triethyl-rosaniline, or triamyl-rosaniline), yields aniline blue (iodine blue). Naphthyl also may be introduced into fuchsin to form, according to Wolff, a brilliant blue colour termed naphthyl blue. Under the names of *Bleu de lumière* or *Bleu de nuit*, is known a blue dye which appears blue in daylight as well as in artificial light. A blue with a violet hue is known as *Bleu de Parme.*

Aniline Green. 4. We are acquainted with two varieties of this colour, viz. aldehyde green and iodine green. The former, also called emeraldine, was discovered in 1863 by Cherpin, chemist in M. Usèbe's Works at Saint Ouen, and is obtained by treating a sulphuric acid solution of sulphate of rosaniline with aldehyde. By cautiously heating this mixture, a deep green pigment is obtained which contains sulphur; the formula of this compound is, according to Dr. A. W. Hofmann, $C_{22}H_{27}N_3S_2O$. When required for use hyposulphite of soda is added and the compound boiled therewith in water; this solution is used for dyeing silk, and instead of the soda-salt sulphuret of ammonium or sulphuretted hydrogen may be used. The green-coloured material can be precipitated by a mixture of common salt and sodic carbonate, while a mixture of 2 parts of sulphuric acid and 50 to 70 parts of alcohol is a solvent for this substance. This aniline green is especially beautiful when seen by candle-light. The other kind of aniline green is the so-called iodine green, discovered (1863) by Dr. A. W. Hofmann, as a by-product of the manufacture of the methylated and ethylated rosaniline violets.

Iodine green is obtained by the following process:—1 part of acetate of rosaniline, 2 of iodide of methyl, and 2 of methylic alcohol, are heated together for several hours under a high pressure, or on the small scale in a sealed tube. When the operation is finished the result is a mixture of violet and green pigments dissolved in methylic alcohol. The volatile substances having been driven off by distillation the mixture of pigments is put into boiling water, wherein the green is completely dissolved, while the violet remains insoluble; the former is precipitated by a cold saturated solution of picric acid in water, the ensuing precipitate—picrate of iodine green—is collected on a filter, rapidly washed with the smallest possible quantity of water, and after having been partly dried, brought into commerce as a paste (*en pâte*). The crystalline iodine green, free from picric acid, has the formula $C_{25}H_{33}N_3OI_2$.

Aniline Yellow. Aniline Orange.

5. By the preparation of the red-coloured pigments from aniline oil, there is formed, as well as fuchsin, a resinous substance, from which Nicholson obtained a brilliant yellow-coloured pigment, the aniline yellow, aniline orange, aurin, or hydrochlorate of chrysaniline, which dyes wool and silk brilliantly yellow. Chrysaniline is a base of the formula $C_{20}H_{17}N_3$. The most interesting salt of this base is the nitrate, which is insoluble in water. The residue of the preparation of fuchsin is treated with steam, and as soon as a portion of the base has been dissolved, it is precipitated by the aid of nitric acid. Schiff obtained aniline yellow by the action of antimonic acid or hydrated oxide of tin upon aniline; M. Vogel obtained a yellow pigment by the action of nitrous acid upon an alcoholic solution of rosaniline. This aniline yellow has the formula, $C_{20}H_{19}N_2O_6$; it is soluble in alcohol, not so in water.

Aniline Black and Aniline Brown.

6. Aniline black, $C_6H_7NO_6$, a deep aniline green formed by the action of oxidising agents upon aniline oil, was observed as early as 1843 by Dr. J. von Fritzsche, and was formerly prepared from the residues of the preparation of aniline violet with bichromate of potash; but now we obtain aniline black by the action of chlorate of potash and chloride of copper upon hydrochlorate of aniline, as recommended by Lightfoot. As has been proved by Cordillot, these two chemical reagents may be replaced by ferricyanide of ammonium; or, according to Lauth, by freshly precipitated sulphuret of copper. According to Bolley, the last substance acts by becoming oxidised to sulphate of copper, and simultaneously carrying oxygen on to aniline. The black made according to this method being insoluble has to be formed on the woven textile fabrics themselves, and is hence also called black indigo or indigo black. More recently, again, the so-called Lucas black (Peterson's black) has been obtained, its most valuable property being that it is a ready made black, which for its full development only requires a weak oxidation. It is a black fluid mass consisting of hydrochlorate of aniline and acetate of copper, which mixed with some starch paste is printed on the fabrics. The black becomes

oxidised by exposure to air; the oxidation is rendered more rapid by ageing the fabrics in a room heated to 40°. Aniline black is used both in dyeing and printing textile fabrics.

7. Aniline brown (Habana brown) is prepared according to de Laire by heating a mixture of aniline violet or aniline blue with hydrochlorate of aniline to 240°, until the mixture becomes brown-coloured The brown thus obtained is soluble in water, alcohol, and acids, and can be at once employed in dyeing. Another kind of aniline brown (Bismark brown) is obtained by fusing fuchsin with hydrochlorate of aniline.

II. *Carbolic Acid Colours.*

Carbolic Acid Dyes. The portion of heavy coal-tar oil which distils over at 150° to 200°, consists chiefly of carbolic acid (phylic acid phenol). As brought into commerce by C. Calvert and Co., C. Lowe and Co., and a great many other eminent firms both in this country and abroad, carbolic acid is a crystalline mass which becomes slightly reddened by exposure to air, fuses at 34°, and boils at 186°. It is prepared according to Laurent's method by treating the heavy oils of tar with alkalies. There are three homologous phenols in this preparation:—

Carbolic acid, C_6H_6O,
Cresylic acid, C_7H_8O.
Phlorylic acid, $C_8H_{10}O$.

Carbolic acid is soluble in 33 parts of water. Calvert's carbolic acid, as used in the colour-works, is prepared by cooling a mixture of the Laurent acid in water. At $+4°$ a hydrate of carbolic acid, $C_6H_6O+H_2O$, is separated, and by elimination of water it becomes *pure* carbolic acid, which fuses at 41°. While carbolic acid is very largely used in several degrees of purity for a variety of purposes as an antiseptic, disinfectant, &c., more than 50 per cent of all the carbolic acid manufactured is used for the purpose of preparing the following pigments and dye materials:—

1. Picric acid.
2. Phenyl brown.
3. Grénat soluble.
4. Coralline.
5. Azuline.

Picric Acid. Picric acid, trinitro-phenylic acid, $C_6H_3(NO_2)_3O$, obtained by the action of nitric acid upon carbolic acid, or better, by treating crystallised phenyl sulphate of sodium with nitric acid. is a yellow substance crystallising in foliated structure, difficultly soluble in cold, readily in hot water, and also soluble in alcohol. It is used for dyeing wool and silk yellow, and with aniline green (iodine green), indigo, and Berlin blue, it is used for dyeing silk and wool green.*

In France annually some 80 to 100 tons of picric acid are prepared, but the bulk is used for the manufacture of the picrate gunpowder (see p. 157). The ammonia salt of the trinitro-cresylic acid is met with in the trade as Victoria yellow as a dye material. When treated with cyanide of potassium, picric acid yields isopurpuric acid, while the trinitro-cresylic acid yields with the same cyanide cresyl-purpuric acid (V. Sommaruga); the potassium and ammonium salts of the respective acids yield the grenate brown.

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* It has of late become usual to employ, instead of pure (non-explosive) picric acid, the soda salt of that acid, under the name of picric acid and aniline-yellow. This has given rise to very serious accidents, owing to the highly explosive nature of the salt.

Phénicienne. 2. Phenyl brown was first prepared by Roth in 1865 by causing nitro-sulphuric acid to act upon carbolic acid; the resulting substance, phénicienne or phenyl brown, is an amorphous powder, a mixture of two pigments, viz., a yellow, according to Bolley, dinitrophenol, $C_6H_4(NO_2)_2O$, and a black-brown substance which is similar to the humus compounds. Phenyl brown is used for dyeing wool and silk.

Grenate Brown. 3. Grénat soluble, which has been very recently introduced by J. Casthelaz in Paris as a substitute for orseille, is nothing more than the well-known isopurpurate of potash, which was first discovered by Hlasiwetz, and is formed by the action of cyanide of potassium upon a solution of picric acid according to the following reaction, as described by Zulkowsky:—

$$\underbrace{C_6H_3(NO_2)_3O}_{\text{Picric acid.}}+\underbrace{3KCN}_{\text{Cyanide of potassium.}}+2H_2O=\underbrace{C_8H_4KN_5O_6}_{\text{Isopurpurate of potash.}}+\underbrace{NH_3}_{\text{Ammonia.}}+\underbrace{KCO_3}_{\text{Carbonate of potash.}}$$

As Grenate brown when dry is explosive with the least friction, it is kept in the state of a paste, to which some glycerine is added for the purpose of keeping it moist.

Corallina. 4. Coralline, or pæonine, a scarlet dye material, is formed, according to Kolbe and R. Schmidt, by heating a mixture of carbolic, oxalic, and sulphuric acids until the colour has been sufficiently developed. When the reaction is finished the mass is washed with boiling water for the purpose of eliminating the excess of acid. The residue is next dried, pulverised, and submitted at 150° to the action of ammonia.

The relation existing between the rosolic acid, discovered in tar by Runge, and coralline is at present not fully established, but according to Caro's researches these substances are identical. Rosolic acid may be formed from carbolic and cresylic acids (as rosaniline is from aniline and toluidine) according to the following formulæ:—

$$\underbrace{C_6H_6O}_{\text{Carbolic acid.}}+\underbrace{2C_7H_8O}_{\text{Cresylic acid.}}=\underbrace{C_{20}H_{16}O_3}_{\text{Rosolic acid.}}+3H_2.$$

Azuline. 5. Azuline (phenyl blue). When coralline is heated with aniline oil (commercial aniline) there is obtained, according to J. Persoz and Guinon-Marnas, a blue pigment, which is termed azuline, or azurine.

Pigment directly from Nitro-benzol. It has been attempted to prepare pigments directly from nitro-benzol. Laurent and Casthelaz state that a red pigment is obtained by keeping a mixture of 12 parts of nitro-benzol, 24 parts of iron-filings, and 6 parts of hydrochloric acid for twenty-four hours at the ordinary temperature of the air. There is formed a solid resinous-like mass, which is first exhausted with water and the solution precipitated with common salt. The pigment thus obtained is said to be a substitute for fuchsin, and as such capable of being used as a dye and for calico-printing.

III. *Naphthaline Pigments.*

Naphthaline. This material, $C_{10}H_8$, was discovered in the year 1820 by Garden in coal-tar, and was afterwards the subject of researches by Faraday, A. W. Hofmann, M. Ballo, and others. According to Berthelot it may be synthetically prepared by substituting for 2 atoms of hydrogen of the benzol 2 atoms of acetylen (C_2H_2):—

$$\underbrace{C_6H_6}_{\text{Benzol.}}-2H+\underbrace{2C_2H_2}_{\text{Acetylen.}}+C_6H_4(C_2H_2)_2=\underbrace{C_{10}H_8}_{\text{Naphthaline.}}.$$

Naphthaline is a crystalline substance, exhibiting rhomboids when in very thin scales. Its odour is peculiar and somewhat similar to that of storax; it has a burning taste. When cooled, after having been fused, it appears as a white crystalline mass having a sp. gr. = 1·151. It fuses between 79° and 80°, and boils between 216° and 218°. When treated with nitric acid, naphthaline yields phthalic acid, which according to circumstances and by elimination of carbonic acid may be either converted into benzol or into benzoic acid:*—

$$\alpha.\ \underbrace{C_8H_6O_4}_{\text{Phthalic acid.}} - 2CO_2 = \underbrace{C_6H_6}_{\text{Benzol.}}$$

$$\beta.\ \underbrace{C_8H_6O_4}_{\text{Phthalic acid.}} - CO_2 = C_7H_6O_2.$$

There exists between the derivatives of benzol and naphthaline a great analogy which not only extends to the composition and reaction, but even to chemical and physical properties. The analogy of composition is exhibited by the following tabulated form:—

Benzol (hydride of phenyl), C_6H_6.	Naphthaline (hydride of naphthyl), $C_{10}H_8$.
Nitro-benzol, $C_6H_5(NO_2)$.	Nitro-naphthaline, $C_{10}H_7(NO_2)$.
Aniline, C_6H_7N.	Naphthylamine, $C_{10}H_9N$.
Rosaniline, $C_{20}H_{19}N_3$.	Base of the naphthaline red, $C_{30}H_{21}N_3$.

Naphthylamine, $C_{10}H_9N_3$, the base which corresponds to aniline, is prepared from naphthaline in exactly the same manner as aniline is prepared from benzol, by converting naphthaline by the aid of nitro-sulphuric acid into nitro-napththaline, which is next converted into napthylamine by Béchamp's process (see p. 574). As proved by M. Ballo (1870) the naphthylamine may be readily eliminated from the reduced mass, treated with iron and acetic acid, by distilling it with the aid of steam. Naphthylamine crystallises in white acicular crystals, fuses at 50°, and boils at about 300°. Its taste is sharp and bitter. It is almost insoluble in water.

Naphthylamine serves for the preparation of the following dyes:—

1. Martius yellow,
2. Magdala red,
3. Naphthaline violet,
4. Naphthaline blue.

Martius Yellow. 1. This pigment, better known in England as Manchester yellow, or naphthaline yellow, *Jaune d'or*, is the calcium or sodium compound of binitro-naphthalinic acid ($C_{10}H_6(NO_2)_2O$), obtained by adding to a solution of hydrochlorate of naphthylamine nitrite of soda until all the napththylamine has been converted into diazonaphthol. The fluid which contains diazonaphthol is next mixed with nitric acid and then heated to the boiling point, the binitro-naphthylic acid is thrown down in yellow acicular crystals. The conversion of naphthylamine into binitro-naphthylic acid (binitro-naphthol) may be elucidated by the following formulæ:—

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* The large quantity of benzoic acid now consumed in the preparation of some of the tar colours, and employed for other chemico-technical purposes, is no longer obtained from the benzoin resin (gum benzoin, as it is often termed); but this acid is prepared either from hippuric acid present in the urine of horses, or it is a derivative from naphthaline. The naphthaline-benzoic acid may be prepared by two different methods, viz.:—1. By converting naphthaline into phthalic acid, and converting this acid, by heating it with lime, into benzoate of lime, from which, by the addition of hydrochloric acid, the benzoic acid is set free and precipitated. 2. By converting phthalic acid into phthalimide, $C_6H_5NO_2$, and converting this substance by distilling it with lime into benzonitrile, C_7H_5N, the latter by boiling with caustic soda solution being converted into benzoate of soda, from which solution the benzoic acid is set free and precipitated by the addition of hydrochloric acid. In the year 1868 Merz obtained from cyannaphthyl a new acid, to which the name of naphtoe acid is given (formula $C_{11}H_8O_2$), a substitute for benzoic acid.

$$\alpha.\ \underbrace{C_{10}H_9N}_{\text{Naphthylamine.}}+HNO_2=2H_2O+\underbrace{C_{10}H_6N_2}_{\text{Diazonaphthol.}}$$

$$\beta.\ \underbrace{C_{10}H_6N_2}_{\text{Diazonaphthol.}}+2HNO_3=2N+H_2O+\underbrace{C_{10}H_6(NO_2)_2O}_{\text{Binitro-naphthylic acid.}}$$

As proved by M. Ballo, the latter acid may be directly formed by the action of nitric acid upon naphthylamine. Manchester yellow imparts directly to wool and silk, without the intervention of any mordant, yellow hues, which may be made to differ in depth of colour from lemon-yellow to deep golden-yellow. 1 kilo. of the dry calcium or sodium compound dyes 200 kilos. of wool brilliantly yellow. While picric acid dye is volatilised by steam, the Manchester yellow perfectly admits of the operation of steaming. In this country this dye material is frequently employed for the purpose of modifying the hue of magenta.

Magdala Red. 2. This pigment, naphthaline red, $C_{30}H_{21}N_3$, was discovered in 1867 by Von Schiendl at Vienna, and has been the subject of researches by Durand, Ch. Kestner, Dr. A. W. Hofmann, and others. It is generated from naphthylamine by the elimination of 3 molecules of hydrogen from 3 molecules of the base:—

$$\underbrace{3C_{10}H_9N}_{\text{Naphthylamine.}}-3H_2=\underbrace{C_{30}H_{21}N_3}_{\text{Magdala red.}}$$

On the large scale the preparation of Magdala red is effected in *two* stages. In the first the naphthylamine is converted into azodinaphthyl-diamine by the action of nitrous acid:—

$$\alpha.\ \underbrace{2C_{10}H_9N+HNO_2}_{\text{Naphthylamine.}} = \underbrace{2H_2O+C_{20}H_{15}N_3}_{\text{Azodinaphthyl-diamine.}}$$

In the *second* stage the azodinaphthyl-diamine is treated with naphthylamine, the result being the formation of Magdala red.

$$\beta.\ \underbrace{C_{20}H_{15}N_3}_{\substack{\text{Azodi-}\\\text{naphthyl-diamine.}}}+\underbrace{C_{10}H_9N}_{\substack{\text{Naphthyl-}\\\text{amine.}}} = \underbrace{C_{20}H_{21}N_3}_{\substack{\text{Magdala}\\\text{red.}}}+NH_3.$$

The Magdala red of commerce, a black-brown, somewhat crystalline powder, is the chloride of a base of the composition described. As regards tinctorial powder Magdala red is not less valuable than fuchsin, while it surpasses the latter in being a very fast colour. When treated with iodide of methyl and iodide of ethyl, naphthaline red yields violet and blue-coloured derivatives.

Naphthaline Blue and Naphthaline Violet. 3 and 4. Violet and blue naphthaline pigments may be prepared in various ways; for instance, by phenylising naphthylising, methylising, or ethylising Magdala red; also by treating naphthylamine with mercuric nitrate (Wilder), by substituting for hydrogen in aniline and toluidine the radical naphthyl, $C_{10}H_7$. J. Wolff, as early as 1867, obtained a very brilliant naphthyl blue in this manner; again, from rosaniline and mono-bromnaphthaline, and from rosaniline and naphthylamine (M. Ballo). Very recently Blumer-Zweifel as well as Kielmeyer have produced naphthylamine violet on cotton and linen fabrics, by treating naphthylamine while present on the woven tissues with chloride of copper, chlorate of potash, and, in fact, all such reagents as may be employed for the production of aniline black* (see p. 579).

IV. *Anthracen Pigments.*

Anthracen Pigments. Anthracen (para-naphthaline, photen), $C_{14}H_{10}$, is present in coal-tar to an amount of 0·75 to 1·0 per cent, and was discovered by J. Dumas in 1831, while in 1869 it was first employed by Graebe and Liebermann for the purpose of obtaining anthracen red or artificial alizarin. Anthracen occurs in that portion of the products of the distillation of coal-tar which being rather thick are known in this country by the designation of *green grease*, and, as such, used as a coarse lubricating material. The green grease consists of heavy oils, some naphthaline, and about 20 per cent of anthracen. By means of the hydro-extractor, and by submitting the raw material to strong pressure, crude (containing 60 per cent pure) anthracen is obtained. This raw material is purified by being treated with benzoline (petroleum spirit), aided by heat, and again aided by the centrifugal machine, fusion, and sublimation, these operations resulting at last in the production of pure anthracen. This substance then appears as small foliated crystals, white, void of odour, fusing at 215°, and subliming at a higher temperature without decomposition. This body is sparingly soluble in alcohol and benzol, more readily in sulphide of carbon. With picric acid it yields a compound exhibiting ruby-red crystals; while under the influence of oxidising agents it is converted into anthrachinon (oxanthracen, oxyphoten), $C_{14}H_8O_2$, which in its turn is converted into alizarine, $C_{14}H_8O_4$, by a circuitous process.

According to the original method of preparing alizarine, the anthrachinon, $C_{14}H_8O_2$, obtained from anthracen by the action of oxidising agents, such as nitric acid, was first converted into bibromide of anthrachinon, $C_{14}H_6Br_2O_2$, by treating anthrachinon with bromine, and this bromated compound was further treated either with caustic potash or caustic soda at a temperature of 180° to 200°, the bibromide of anthrachinon becoming converted into alizarine potassium (or alizarine sodium, if caustic soda has been used), from which the alizarine is set free by the addition of hydrochloric acid:—

$$\alpha.\ \underbrace{C_{14}H_6Br_2O_2}_{\substack{\text{Bibromide of}\\ \text{Anthrachinon.}}}+KOH=\underbrace{C_{14}H_6K_2O_4}_{\substack{\text{Alizarine}\\ \text{Potassium.}}}+2BrK+2H_2O.$$

$$\beta.\ \underbrace{C_{14}H_6K_2O_4}_{\substack{\text{Alizarine}\\ \text{Potassium.}}}+2ClH=\underbrace{C_{14}H_8O_4}_{\text{Alizarine.}}+2ClK.$$

Alizarine is now prepared from anthrachinon by treatment at a temperature of 260° with concentrated sulphuric acid of 1·84 sp. gr., the anthrachinon being converted into a sulpho-acid; this acid is next neutralised with carbonate of lime, the fluid decanted from the deposited gypsum, and carbonate of potash added to it for the

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[*] It is evident that by combining suitable aniline, naphthyl, and cetyl compounds, the greatest variety of blue and violet pigments may be prepared. The following blue pigments were obtained in the summer of 1867, these researches being undertaken in consequence of the results obtained by J. Wolff in the same direction. 1. Fuchsin and bromide of naphthyl. 2. Fuchsin and cetyl bromide. 3. Naphthylamine, fuchsin, and aniline oil. 4. Cetylamine, fuchsin, and aniline oil. 5. Naphthylamine, fuchsin, and cetylamine. 6. Cetylamine, fuchsin, and naphthylamine.

purpose of precipitating all the lime. The clear liquid is then evaporated to dryness, the resulting saline mass is converted into alizarine-potassium by heating it with caustic potash. From the alizarine-potassium thus obtained the alizarine is set free by the aid of hydrochloric acid. According to another method, the preparation of anthrachinon is avoided, and anthracen employed directly, by first converting it—by the aid of sulphuric acid and the application of heat—into anthracen sulpho-acid, $C_{28}H_{18}SH_4O_3$. After having been diluted with water, the solution of this acid is treated with oxidising agents (peroxides of manganese, lead, chromic acid, nitric acid), and the acid fluid is next neutralised with carbonate of lime. When peroxide of manganese has been used the manganese is also precipitated as oxide. The oxidised sulpho-acid having been previously converted into a potassium salt, the latter is heated with caustic potash, alizarine-potassium being obtained.

There is no doubt that anthracen may be converted into alizarine by other means; and it is very likely that from other hydrocarbons (benzol, toluol, naphthalin) present in coal-tar, anthracen and anthracen red may be obtained.

The industrial manufacture of artificial alizarine, carried on in the first place by the inventors of this process—Graebe and Liebermann; and taken up by J. Gessert, at Elberfeld; Brönner and Gutzkow, at Frankfort-on-Maine; Brüning, at Höchst (near Wiesbaden); Greiff, at Cologne; and by Perkin, in London—is one of the brightest pages in the history of chemical technology. Although for the present anthracen red cannot compete with madder, it will, in all probability, become in a very great measure a substitute for that dye-stuff and garancine.

V. *Pigments from Cinchonine.*

Cinchonine Pigments. The preparation of pigments from cinchonine—an almost waste by-product of the manufacture of quinine on the large scale—may be conveniently considered as an appendix to the coal-tar colours. Cinchonine is submitted to distillation with hydrate of soda in excess, the resulting product being about 65 per cent crude chinoline (chinoline oil), a mixture of the three following homologous bases:—

Chinoline … … … … … …	C_9H_7N.
Lepidine … … … … … …	$C_{10}H_9N$.
Kryptidine or dispoline … … …	$C_{11}H_{11}N$.

Lepidine is the chief constituent of this mixture.

When chinoline oil is heated with iodide of amyl the result is the formation of amyl-lepidin-iodide, which on being treated with caustic soda solution, yields a very brilliant blue pigment—cyanine, lepidine blue, or chinoline blue, $C_{30}H_{39}N_2I$. This substance is a crystalline compound, exhibiting a metallic green gloss and golden yellow hue; it is difficultly soluble in water, readily in alcohol. The formation of cyanine may be elucidated by the following formulæ:—

$$\alpha.\ \underbrace{C_{10}H_9N}_{\text{Lepidine.}}+\underbrace{C_5H_{11}I}_{\substack{\text{Iodide of}\\ \text{Amyl.}}}=\underbrace{C_{15}H_{20}NI.}_{\substack{\text{Amyl-lepidin-}\\ \text{iodide.}}}$$

$$\beta.\ \underbrace{2C_{15}H_{20}NI}_{\substack{\text{Amyl-lepidin-}\\ \text{iodide.}}}+NaOH=\underbrace{C_{30}H_{39}N_2I}_{\text{Cyanine}}+CaI+H_2O.$$

Red Pigments occurring in Plants and Animals.

Red Dye Materials. Madder.

Madder is the root of the *Rubia tinctorum*, a perennial plant cultivated in Southern, Central, and Western Europe; while in the Levant the *R. peregrina*, and in the East Indies and Japan the *R. mungista* (mungeet), are partly cultivated, partly met with in the wild state. According to the researches made in England, the dye imported under the name of mungeet from India is not the root, but the reedy stem of a species of *Rubia*, and as a dye it is inferior. The native country of the madder plant is the Caucasus. All these plants are perennial. The root varies in length from 10 to 25 centims.; it is not much gnarled, and is generally a little thicker than the quill of a pen. Externally the root is covered with a brown bark; internally it exhibits a yellow-red colour. Madder is met with in the trade in the root (technically *racine* if European), and in powder exhibiting a red-yellow colour, and possessing a peculiar odour. Avignon madder, however, has hardly any smell at all; but the odour is particularly marked in Zeeland, or so-called Holland, madder. The powdered madder is always kept in strong oaken casks, so as to exclude air and light. The best kind of madder is that grown in the Levant (Smyrna and Cyprus), and met with in the trade under the name of *lizari* or *alizari*, in roots which are usually rather thicker than the roots of the European varieties, owing partly to the fact that the Levant madder is generally of four to five years' growth, while in Europe the roots are of two to three years' growth only. Dutch madder, chiefly grown in the province of Zeeland, is met with decorticated (*robé*), the outer bark and sometimes the splint bark having been removed. The well dried roots are broken up by means of wooden stampers moved by machinery, to reduce the bark and splint bark to powder, while the very hard internal portion of the root is left untouched, this being separated from the powder by means of sieves. The powder is put into casks and termed *beroofde*. During the last ten or twelve years, the old madder sheds (*meestoven*) in Zeeland have been superseded by large manufactories, in which the madder root is treated as it is in the Vaucluse (France), and ground up entirely, so that the former distinct qualities of madder are no longer met with. When the whole root is pulverised the madder is termed *onberoofde, non robé*. Besides the Dutch madder, that from Alsace and from the Vaucluse, Avignon, occur very largely in the trade. What is known as *mull* madder is the refuse and dust from the floors of the works, and is the worst quality. In addition to colouring matter, madder contains a large quantity of sugar, of which W. Stein (1869) found as much as 8 per cent. While it was formerly considered that madder contained no less than five different colouring substances, it appears from recent researches that this root in fresh state only contains two pigments, viz. ruberythrinic acid (formerly termed xanthin), and purpurine. According to Dr. Rochleder, the former of these is converted under the influence of a peculiar nitrogenous substance present in the madder root into alizarine—the essential colouring matter of madder—and into sugar:—

$$\underbrace{C_{20}H_{22}O_{11}}_{\text{Ruberythrinic acid.}} = \underbrace{C_{14}H_8O_4}_{\text{Alizarine.}} + \underbrace{C_6H_{12}O_6}_{\text{Sugar.}} + H_2O.$$

According to the researches of Graebe and Liebermann, alizarine is a derivative from anthracen, $C_{14}H_{10}$, the formula of the former being $C_{14}H_8O_4$. As already mentioned (see p. 585), Graebe and Liebermann have succeeded in converting anthracen into alizarine (1869). Alizarine is yellow, but becomes red under the influence of alkalies and alkaline earths. Madder contains a red pigment, purpurine, or rubiacine, $C_{14}H_8O_3$, which by itself, as well as in combination with alizarine, yields a good dye.

Madder Lake. We understand by this term a combination of alizarine and purpurine (the colouring matter of madder) with basic alumina salts. Madder lake is prepared by first washing madder with water, distilled or at least free from lime salts, and next exhausting the dye-stuff with a solution of alum, the liquor thus obtained being precipitated with carbonate of soda or borax. The bulky precipitate having been collected on a filter is thoroughly washed and dried.

Flowers of Madder. The preparation made from madder on the large scale and known in the trade as flowers of madder (*fleur de garance*), is obtained from the pulverised madder by steeping it in water, inducing fermentation of the sugar contained in it, and next thoroughly washing the residue, first with warm, next with cold water. The residue after subjection to hydraulic pressure to remove the water, is dried at a gentle heat, and having been pulverised again is used in the same manner as madder for dyeing purposes. The operation of dyeing with the flowers of madder requires a less elevated temperature of the contents of the dye-beck. It would appear that by the preparation of the flowers of madder the pectine substances of the root are eliminated which otherwise become insoluble during the operation of dyeing.

Azale. When flowers of madder are treated with boiling methylic alcohol (wood-spirit), the solution obtained filtered, and water added to the filtrate, a copious yellow precipitate is obtained, which having been washed with water and dried constitutes the material known as azale (from *azala*, Arabian for madder), which has been suggested for use as a dye material in France. Probably this substance is crude alizarine; as obtained from madder or garancine it is met with in the trade sometimes under the name of Pincoffine, having been first discovered and prepared by Mr. Pincoffs, at Manchester.

Garancine. This preparation of madder contains the colouring principles of the root in a more concentrated, pure, and more readily exhaustible state. In order to prepare garancine, madder (generally this term is given to the pulverised root) is first moistened uniformly with water, and next there is added ½ part of sulphuric acid diluted with 1 part of water. This mixture is heated by means of steam to about 100° for one hour, and the magma then thoroughly washed with water for the purpose of eliminating all the acid. This having been done the garancine is submitted to hydraulic pressure for the purpose of getting rid of the greater part of the water, after which the material is dried and lastly ground to a very fine powder. By the action of the sulphuric acid, some of the substances contained in madder and more or less interfering with its application as a dye, are eliminated by the washing of the garancine, while the colouring matter remains mixed with the partly carbonised organic substances. As regards its tinctorial value 1 part of garancine may be taken as equal to 3 to 4 parts of madder. As madder when employed in dyeing does not become quite exhausted, the fluids of the dye-beck are **Garanceux.** strained from the solid residue, and this is treated with half of its weight of sulphuric acid. The mass is next treated as has been described under Garancine, and constitutes after drying what is known as *garanceux*, being used generally for the production of what are termed *sad* colours (black, deep brown, lilac). As a matter of course garanceux is of less tinctorial value than garancine.

Colorine. The substance met with in commerce under the name of colorine is the dry alcoholic extract of garancine, and consists essentially of alizarine, purpurine, fatty matter, and other substances soluble in alcohol present in garancine. E. Kopp commenced some years since to exhaust madder with an aqueous solution of *sulphurous* acid, thereby obtaining the pigments of madder in a (for technical purposes) pure condition. These preparations, which are already extensively used, are distinguished as:—Green alizarine (*Alizarine verte*), which from Alsace madder is obtained to an amount of about 3 per cent, containing with the alizarine a green resinous material; yellow alizarine (*Alizarine jaune*), the former substance without the resinous material, this having been eliminated by suitable solvents, as purpurine and flowers of madder. The tinctorial value of purpurine amounts to 10 times, and that of the green and yellow alizarine to 32 to 36 times, that of madder. Madder of good quality yields on the large scale:—

Purpurine	1·15 per cent.
Green alizarine	2·50 ,,
Yellow alizarine	0·32 ,,
Flowers of madder	39·00 ,,

Brazil or Camwood. By this name are designated several varieties of wood belonging to the *Cæsalpinia*, and used for dyeing purposes. The best kind is the so-called Pernambuco or Fernambuco wood, obtained from the *Cæsalpinia brasiliensis s. crista*; externally it is yellow-brown, internally its colour is a bright red, while the wood is heavy and rather hard. Its name is derived from that of the state of the Brazilian Empire, in which the tree grows abundantly. It is met with in commerce in chips and large logs. The sapan wood obtained from Japan, and derived from the (*C. sapan*) is an inferior kind, while the varieties known as Lima or Nicaragua wood, or *Bois de Ste. Marthe* (*C. echinata*), and the brasilet wood (*C. vesicaria*), are all of less value. All these kinds of wood contain a colouring matter termed brasiline, (according to Bolley the formula is $C_{44}H_{40}O_{14}+3H_2O$), a colourless substance, crystallising in small acicular crystals, the aqueous solution of which turns gradually carmine-red by exposure to air, a change brought on almost instantaneously either by boiling the solution or by the action of alkalies. Brazil wood is used in dyeing for the production of a beautiful red colour, which is not fast. This wood is also used for the preparation of round lac, for which purpose, however, the red and violet tar-colours are now more often employed. Red ink is commonly made with brazil wood according to the following recipe:—Brazil wood, 250 grms.; alum, 30 grms.; cream of tartar, 30 grms.; water, 2 litres. Boil down to 1 litre, strain the liquid, and next add of gum arabic and sugar candy each 30 grms. A better red ink is obtained by dissolving 2 decigrammes (4 grains) of carmine in 18·27 grms. (5 drms.) of liquid ammonia, and adding a solution of 1 grm. (18 grains) of gum arabic in 2 fluid ounces of water. Red inks are now frequently prepared from solutions of fuchsin to which some gum and alum are added, or by dissolving commercial aurine, a modification of rosolic acid, in a solution of carbonate of soda.

Sandal Wood. There is a red and a yellow variety of this wood in commerce. The red wood is derived from *Pterocarpus santalinus*, a tree growing in Ceylon and other parts of India. The wood is imported in logs exhibiting a straight fibrous texture, and externally a deep red, internally a bright red. The colouring matter contained in this wood is of a resinous nature and is named santaline. According to the researches of H. Weidel (1869), sandal wood contains a colourless body, santal, $C_8H_6O_3$, which appears to be converted by oxidation into santaline. Sandal wood is used for the preparation of coloured lakes, coloured furniture polish, for dyeing wool brown, dyeing leather red, as a pigment in tooth powders, &c. The same pigment is found in barwood, derived from *Baphia nitida*, an African tree; this wood is said to contain no less than 23 per cent of santaline, while sandal wood only contains 16 per cent of this substance.

Safflower. The drug to which this name is given consists of the dried petals of the flowers of the *Carthamus tinctorius*, a thistle-like plant belonging to the family of the *Synantherea*, a native of India, and cultivated in Egypt, the southern parts of Europe, and also to some extent in parts of Germany. Safflower contains a red matter, carthamine, insoluble in water, and also a yellow substance soluble in that liquid. The quality of this drug is better according to its greater purity from mechanical admixtures, such as seeds, leaves of the plant. Carthamine, $C_{14}H_{16}O_7$, or *Rouge végétal*, is prepared in the following manner:—The safflower is exhausted with a very weak solution of carbonate of soda, and in this fluid strips of cotton-wool are dipped, after which the strips are immersed in vinegar or very dilute sulphuric acid for the purpose of neutralising the alkali. The red-dyed cotton strips are next washed in a weak solution of carbonate of soda, and the solution thus obtained is precipitated with an acid; the carthamine thrown down is first carefully washed, and next placed on porcelain plates for the purpose of becoming dry. Carthamine when seen in thin films exhibits a gold-green hue, while when seen against the light the colour is red. When carthamine has been repeatedly dissolved and precipitated it is termed safflower-carmine. Mixed with French chalk (a silicate of magnesia), carthamine is used as a face powder. Safflower is used for dyeing silk, but the red colour imparted is, although brilliant, very fugitive.

Cochenille, or Cochineal. This substance is the female insect of the *Coccus cacti*, found on several species of cacti, more especially on the Nopal plant and the *Cactus opuntia*. This insect and the plants it feeds on are purposely cultivated in Mexico, Central America, Java, Algeria, the Cape, &c. The male insect, of no value as a dye material, is winged, the female wingless. The female insects are collected twice a year after they have been fecundated and have laid eggs for the reproduction of young, and are killed either by the aid of the vapours of boiling water or more usually by the heat of a baker's oven. Two varieties of cochineal are known in commerce, viz., the fine cochineal or *mestica*, chiefly gathered in the district of Mestek, a province of Honduras, on the Nopal plants there cultivated; and the wild cochineal, gathered from cactus plants which grow in the wild state. This latter variety is of inferior quality. Cochineal appears as small deep brown-red grains, at the lower and somewhat flattened side of which the structure of the insects is somewhat discernible. Sometimes the dried insect is covered with a white dust, but frequently the material is met with exhibiting a glossy appearance and black colour. The white dust, very frequently fraudulently imparted by placing the grain with French chalk or white-lead in a bag, is according to the results of microscopical investigation, the excrement of the insect, exhibiting when seen under the microscope the shape of curved cylinders of very uniform diameter and a white colour. Cochineal contains a peculiar kind of acid—carminic acid—which, by the action of very dilute sulphuric acid and other reagents, is split up into carmine-red (carmine)—also present in the insect, together with the acid—and into dextrose:—

$$\underbrace{C_{17}H_{18}O_{10}}_{\text{Carminic acid.}}+3H_2O=\underbrace{C_{11}H_{12}O_7}_{\text{Carmine-red.}}+\underbrace{C_6H_{12}O_6}_{\text{Dextrose.}}$$

What is commonly termed carmine is prepared by exhausting the cochineal with boiling water; to the decanted clear fluid alum is added, after which it is left standing. By another method carmine is prepared by exhausting the pulverised cochineal with a solution of carbonate of soda, white of egg is next added to this solution for the purpose of clarifying it, and afterwards the solution is precipitated with an acid. The washed precipitate is next dried at 30°. So prepared, a finer and better kind of carmine is obtained, but the common carmine—carmine lac and round lac—is prepared by treating an aluminous solution of cochineal with carbonate of soda; the larger the quantity of alumina contained in these preparations, the coarser the quality.

Lac Dye. This dye-stuff is obtained from a resinous substance, stick or grain lac, or gum resin, and is derived from a variety of the cochineal insect in the following manner:—The *Coccus laccæ*, a native of India, pierces the branches of certain kinds of fig-trees from which a milky juice exudes, which, while becoming inspissated, encloses the insects and at last forms a hard resinous mass tinged with the dye-stuff contained in the insects. This pigment is extracted from the resinous matter by means of a solution of carbonate of soda, and the solution obtained is precipitated by alum solution. The lac dye is not very different from cochineal. The dye materials contained in kermes (*Coccus ilicis*), *Coccus polonicus*, and *Coccus fabæ* are similar to that contained in cochineal, but are now quite obsolete; even cochineal is far less used since the coal-tar colours have been introduced.

Orchil and Persio. By orchil, persio, and cudbear, we designate red dye-stuffs which are met with in commerce in pasty masses. Orchil is prepared from several kinds of sea-weed, *Roccella tinctoria*, *R. fuciformis*, *R. Montagnei*, *Usnea barbata*, *Usnea florida*, *Lecanora parella*, *Unceolaria scruposa*, *Ramalina calicaris*, *Gyrophora pustulata*, and others, which having been well dried, are first ground to a very fine powder. This is mixed with urine and left to enter into putrefactive fermentation. The carbonate of ammonia formed by the decay of the urine acting upon the peculiar acids—lecanoric, alpha and beta orcellic, erythrinic, gyrophoric, evernic, usninic, &c.—contained in these sea-weeds converts these non-nitrogenous substances into orcine, $C_7H_8O_2$, this reaction being accompanied by the elimination of water, and usually also with the elimination of carbonic acid. By taking up nitrogen and oxygen orcine is converted into orceine, $C_7H_7NO_3$, constituting the essential colouring matter of orchil. This substance appears as a red paste, exhibiting a peculiar violet odour (*viola odorata*) and an alkaline taste. Before the coal-tar colours were discovered, this dye material was prepared chiefly in England and France, from weeds imported from the Canary Islands, or collected on the Pyrenees and imported from Lima and Valparaiso. Persio, cudbear, or red indigo, is much the same kind of product as orchil; the former was formerly prepared in Scotland from sea-weeds found on the coast. At a later period it was made in large quantity in Germany, in France, and in England. Persio was a red-violet powder. Some ten years ago two preparations of orchil were brought into commerce under the names of orchil carmine and orchil purple (*pourpre Français*). These substances contained the orchil dyes in a very pure condition. Since the tar-colours have made their appearance, the dyes obtained from the sea-weeds, very beautiful but very perishable colours, have in a great measure become obsolete.

Less Important Red Dyes. Among the less important red dyes and colouring matters are the alkanet root (*Anchusa tinctoria*); dragon's blood, a red-coloured resin from *Dracaena draco;* harmala red from the seeds of the *Peganum Harmala*, a plant growing in the Steppes of Russia; Chica red, or carajura, from the leaves of the *Bignonia chica*, a tree growing in Venezuela; purple-carmine, or murexide, obtained from uric acid by treating it with oxidising substances (nitric acid for instance) and next with ammonia.

Blue Dye Materials.

Blue Dye Materials. Indigo. Indigo is the chief blue dye. Although known to the Romans and Greeks, who used it for painting purposes, it was not used as a dye stuff in Europe until about the middle of the sixteenth century. Indigo is a substance which is widely-dispersed in the vegetable kingdom. It is found in large quantity in the leaves of several species of the anil plants, *Indigofera*, belonging to the family of the *Papilionaceæ*. Indigo is also met with in woad, *Isatis tinctoria, Nerium tinctorium, Marsdenia tinctoria, Polygonum tinctorium, Asclepias tingens*, &c. The indigo is not met with in the plants ready formed, but is generated when the freshly-pressed juice of the plant is exposed to the action of the atmosphere.

According to the results of a series of experiments, it appears that in the living plant the colourless pigment is present in combination with a base, lime or an alkali. Dr. Schunck states that the indigo plant contains a material which he has termed indican, which either by fermentation or by the action of strong acids is converted into indigo blue and a peculiar kind of sugar, indigo glycine, according to the following formula:—

$$\underbrace{C_{52}H_{62}N_2O_{34}}_{\text{Indican.}}+4H_2O+\underbrace{C_{16}H_{10}N_2O_3}_{\text{Indigo blue.}}+\underbrace{6C_6H_{10}O_6}_{\text{Indigo glycine.}}.$$

The indigo of commerce is prepared from the indigo plants in the East and West Indies, Southern and Central America, Egypt, and other parts. In Hindostan indigo is prepared from the *Nerium tinctorium*. The following five varieties of the indigo plant are more particularly employed for the preparation of this dye material; the plants are:—*Indigofera tinctoria, I. anil, I. disperma, I. pseudotinctoria*, and *I. argentea*. The plant requires a warm climate and a soil so situated that it is not liable to become inundated. When the plants have grown to maturity they are cut down with a sickle close to the soil and transferred to the factory, where the indigo is extracted from the plant by the following process:—The factory is fitted with large water tanks, filtering apparatus, presses, a cauldron, drying-room, and, lastly, with fifteen to twenty tanks of brickwork laid in hydraulic cement and plastered inside with the same material. Into these tanks the branches, twigs, and the leaves are placed, and water is run in, care being taken to force the green plants down under the water by the aid of stout wooden balks wedged tight against the sides of the tanks. At the usual high temperature of the air in the tropical regions fermentation soon sets in, and the liquid contained in the tanks assumes a bright straw-yellow or golden-yellow colour, a large quantity of gas is evolved, and after a lapse of nine to fourteen hours, the liquid, having become of a deeper yellow hue, or almost the colour of sherry wine, is run from the fermenting tanks into a very large tank of similar construction, into which, when as full as may be judged convenient, a number of workmen enter, provided with long bamboo poles, and commence stirring the fluid vigorously for the purpose of exposing it as much as possible to the action of the air. During this operation, continued for some two or three hours, the colour of the liquid gradually changes to pale green, and the indigo may then be seen suspended in the liquid in very small flocks. The liquid is then left to stand, and the suspended matter gradually subsiding, the water is gradually run off by the aid of taps or plugs fitted into the tank at different heights. At last the somewhat thick, yet fluid, precipitate of indigo is run into a cauldron, where it is boiled for about twenty minutes in order to prevent it fermenting a second time, for by this second fermentation it would be rendered useless. The magma is left in the cauldron over night and the boiling resumed next day and then continued for three to four hours, after which the indigo is run on to large filters, consisting first of a layer of bamboo, next mats, and on these stout canvas, all placed in a large masonry tank. Upon the canvas is left a thick, very deep blue, nearly black paste, which is thence taken and put into small wooden boxes, perforated with holes and lined with canvas; a piece of canvas is put on the top of the paste, and next a piece of plank is fitted closely into the box. So arranged, a number of these are placed under a screw-press for the purpose of eliminating, by a gradually increased pressure, the greater portion of the water, and thus to solidify the pasty material. On being removed from these boxes the cakes of indigo are transferred to the drying-room, and there, daylight and direct sunlight being carefully excluded, gently dried by the aid, in some cases, of artificial heat. In order to prevent the cracking of the cakes, the drying has to be effected very gently, and lasts usually for some four to six days. The dried cakes of indigo are next packed in stout wooden boxes and then sent into the market. The exhausted plants are used for a manure, for although the boughs on being planted in the soil would again grow, they would not yield either in quality or quantity enough indigo to pay the expenses of culture. 1000 parts of fluid from the fermenting tanks yield 0·5 to 0·75 parts of indigo.

Properties of Indigo. The indigo met with in commerce exhibits a deep blue colour, dull earthy fracture, and when rubbed with a hard substance (the better kinds of indigo even when rubbed with the nail of the thumb), give a glossy purplish-red streak. In addition to a larger or smaller quantity of mineral substances, indigo contains a glue-like substance, or indigo glue; a brown substance, indigo brown; a red pigment, indigo red; and the indigo blue, or indigotine, $C_{16}H_{10}N_2O_3$, the peculiar dye material for which the drug is valued. The quantity of indigo blue contained in the several kinds of indigo of commerce varies from 20 to 75 and 80 per cent, and averages from 40 to 50 per cent. Indigo may be purified according to Dumas's process by digestion in aniline, whereby the indigo red and indigo brown pigments are dissolved and eliminated. According to Dr. V. Warther (see "Chemical News," vol. xxiii., p. 252), Venetian turpentine, boiling paraffin, spermaceti, stearic acid, and chloroform, are, at high temperatures, solvents for indigo blue. (See also "Chemical News," vol. xxv., p. 58, "On the Solubility of Indigo (Indigotine) in Phenic Acid.")

Testing Indigo. The quality of indigo is ascertained by its deep blue colour and lightness (see "Chemical News," vol. xxiv., p. 313). G. Leuchs found that in forty-nine samples of this material the best contained 60·5 per cent, the worst 24 per cent of indigotine, the specific gravity of the former being low and of the latter high. Indigo should float on water, and when of good quality it should not, on being broken to pieces, deposit at the bottom of the vessel filled with water in which it is contained a sandy or earthy sediment. On being ignited, indigo should leave only a comparatively small quantity of ash. When suddenly heated, indigo should give off a purplish-coloured vapour, sublimed indigotine, and the drug should be perfectly soluble in fuming sulphuric acid, yielding a deep blue fluid. That kind of indigo which on being rubbed with a hard body exhibits a reddish coppery hue is termed coppery-tinged indigo, *indigo cuivré*. In order to test indigo more accurately, a weighed portion is dried at 100° for the purpose of ascertaining the quantity of hygroscopic water contained, which should not exceed from 3 to 7 per cent. Next the dried indigo is ignited for the purpose of ascertaining the quantity of ash it yields. For good qualities of the drug this amounts to 7 to 9·5 per cent. Numerous methods have been proposed by practical dyers as well as by scientific men for the purpose of ascertaining the value of indigo; that is to say, the quantity of indigotine it contains. Some of these processes are either too tedious, and cause great loss of time, or are not sufficiently exact. A commercial sample of indigo may be treated first with water, next with weak acids, then with alkaline solutions and alcohol, and the ash and hygroscopic water having been estimated, the residue of the different operations will be the indigotine, the process being based upon the insolubility of the latter in the different solvents used for the removal of the impurities met with in the sample under examination. Mittenzwei proposes to reduce the indigo by means of an alkali and protosulphate of iron, to pour over the surface of the liquid a layer of petroleum oil for the purpose of excluding air, to take by the aid of a curved pipette a known bulk of the indigo-containing fluid, and to introduce this fluid at once into a test-jar placed over mercury, and containing a known and accurately measured bulk of pure oxygen. As 1 grm. of white indigotine (soluble) requires for its conversion into blue (insoluble) indigotine 45 c.c. of oxygen, the quantity of gas absorbed gives the quantity of indigotine. This method yields very correct results, but requires an experienced manipulator.

Berzelius's Indigo Test by Reduction.

Take 5 grms. of pure quick-lime prepared from white marble or from well-washed oyster-shells, put the quick-lime into a porcelain mortar, and mix the lime with sufficient water to form a thin milk of lime; next take 5 grms. of the sample of indigo very finely powdered, and add it to the milk of lime, mixing thoroughly, and then pouring the fluid into a flask capable of containing 1200 c.c. Rinse the mortar with water so as to make up a bulk of 1 litre, next add to the contents of the flask 10 grms. of crystallised sulphate of iron, and immediately after cork the flask and let it stand for several hours in a moderately warm place or on a sand-bath, taking care to shake the vessel frequently. After the liquid has become cool and the sediment deposited, a small syphon of known cubic capacity is filled with distilled water, and by the aid of this instrument 200 c.c. of the fluid contained in the flask are transferred to a beaker-glass. Some pure hydrochloric acid having been added to the fluid, it is left to be acted upon by the air until the reduced and soluble indigotine has become insoluble and blue-coloured. The precipitate is collected on a tared filter, well washed, dried, and next weighed. This weight corresponds to the quantity of pure indigo blue present in 1 grm. of the sample.

Penny's Test.

This test is based upon the application of bichromate of potash and hydrochloric acid. 10 parts of finely-pulverised indigo are digested with twelve times its weight of fuming sulphuric acid at a temperature not exceeding 25° for a period of twelve hours. When the indigo has been entirely dissolved the fluid is poured into 1 pint (= 0·568 litre) of water, next 24 grs. of concentrated hydrochloric acid are added, and the fluid is then gently heated, after which it is titrated with a solution of bichromate of potash in water, this solution being added as long as a drop of the fluid taken with a glass rod and placed on a piece of white filtering-paper exhibits a trace of green or blue colouring matter. The operation is finished when the liquor tested exhibits a bright brown or ochrey-yellow speck upon the filtering-paper. 8½ parts of bichromate are required for decolourising 10 parts of pure indigo blue. Chloride of iron may be used for converting indigo blue into isatine. Probably the observation made by Stockvis at Amsterdam (1868), that indigo blue is soluble in chloroform, might be rendered available for the testing of indigo.

Indigo Blue. This substance, also known as indigotine, may be obtained from the indigo of commerce, either by carefully conducted sublimation, or, as already stated, by treating indigo with lime, protosulphate of iron, and water. The formula of indigo blue is $C_{16}H_{10}N_2$. When indigo blue is, in the presence of alkaline substances, brought into contact with bodies which readily absorb oxygen—for instance, with protosulphate of iron, sulphites, &c.—there is formed, with simultaneous decomposition of water, white indigo or reduced indigo, $C_{16}H_{12}N_2O_2$. The use of indigo as a dye material is in great measure based upon this reduction. By the action of oxidising substances, such as permanganic acid, chlorine, chromic acid, a mixture of so-called red prussiate of potash (ferricyanide of potassium) with potash, soda, oxide of copper, &c., indigo blue is converted into isatine, $C_{16}H_{10}N_2O_4$. Indigo blue dissolves in concentrated sulphuric acid, but becomes thereby radically changed and cannot be brought back to its primitive state, forming as it does with the acid a chemical compound—sulphindigotic acid, or, as it is termed by dyers, sulphate of indigo. When this acid solution is treated with carbonate of potash, there is formed indigo carmine or blue carmine, soluble indigo, a deep blue precipitate soluble in 140 parts of cold water. This indigo-carmine is used as a water-colour pigment; while mixed with some starch and a little gum-water it is formed into balls or other suitable shapes and used as washing-blue, ultramarine being also employed for the same purpose.

Logwood, or Campeachy. This dye material is the wood, freed from bark and splint, of the logwood tree, *Hæmatoxylon campechianum*, a native of Central America, and cultivated in several of the West Indian Islands. The colouring matter contained in this wood is called hæmatoxyline, $C_{16}H_{14}O_6$, a pale yellow, transparent, aciculated crystalline body. By itself it is not a pigment, but is a colourable material, which becomes coloured when brought into contact with strong alkalies, more especially with ammonia and the oxygen of the air. The solution of hæmatoxyline in water is quite colourless, but becomes at once purple-red by the smallest addition of ammonia. The colouring matter thus formed is termed hæmateine. Logwood is used for the purpose of dyeing blue and black. Extract of logwood is very frequently prepared. As with other similar extracts, it should be made in vacuum pans withdrawn from the oxidising action of the air, because the hæmatoxyline contained in logwood becomes thereby altered. The makers of the extracts of dye-woods invariably use vacuum apparatus.

Litmus. This colouring matter, also sometimes termed tournesol, is only very rarely used as a dye for textile fabrics, the colour imparted being very fugitive; but litmus is employed to impart a bluish tinge to whitewash-lime, further for colouring test-papers, for giving a red hue to the red champagnes, &c. Litmus is obtained from the seaweeds that yield archil, cudbear, and persio, potash being employed with the ammoniacal liquor. The difference in the preparation consists in the fermentation and oxidation being carried further, the result being that the red pigment (orcin) is thereby converted into a blue-coloured material azolitmine:—

$$\left.\begin{array}{l}\text{Orcin, } C_7H_8O_2\\ \text{Ammonia, } NH_3\\ \text{Oxygen, } 4O\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Azolitmine, } C_7H_7NO_4\\ \quad\text{and}\\ \text{Water, } 2H_2O.\end{array}\right.$$

The fermented mass is mixed with gypsum and chalk, moulded into lozenges, dried, and sent into commerce.

That known as litmus on rags, *tournesol en drapeaux,* is prepared in the southern parts of France (almost exclusively at Grand Gallargues, Département du Gard) from the juice of the *Croton tinctorium* in which coarse linen rags are repeatedly steeped, and these having been submitted to the action of the ammonia evolved from stable manure or from lant, become purple-red coloured. Weak acids turn this colour to yellow-red, which is not again turned to purple-blue by alkalies, the effect of these being to render the colour somewhat green. The tournesol en drapeaux is largely used in Holland for imparting a colour to the crust of certain kinds of cheese made in that country, the effect being that the cheese thus externally dyed is by far less liable to decay and to be attacked by cheese-mites. The pigment is also used for colouring a peculiar kind of paper, extensively employed for the covering of sugar-loaves. It is also used for imparting a tinge to liqueurs, sweetmeats, &c.

Yellow Dyes.

Yellow-Wood, Fustic. Yellow-wood is the hard wood of the dyer's mulberry tree, botanically termed *Morus tinctoria* or *Maclura aurantiaca.* It is imported chiefly from Cuba, San Domingo, and Hayti. This wood has a yellow and in some parts yellow-red colour, due to a colourless crystalline body, morine, $C_{12}H_8O_5$, present in combination with lime, and also to a peculiar kind of tannic acid, morine-tannic acid, also termed maclurine (formula, $C_{13}H_{10}O_6$), both often met with deposited in the wood in large quantities. Morine becomes yellow by exposure to air and the simultaneous influence of alkalies. When treated with caustic potash maclurine is split up into phloroglucine and protocatechutic acid. Yellow-wood is employed for dyeing yellow and also black, in consequence of the large quantity of tannic acid it contains. The commercial extract of this wood is termed cuba extract.

Young Fustic, French Fustet. This is a green-yellow wood, exhibiting brown-coloured stripes, and derived from a European shrub, the *Rhus cotinus* of the botanists, a plant belonging to the southern parts of Europe. The prefix "young" is given to it on account of the smallness of its branches as compared with that of the yellow-wood, which is distinguished as old fustic. The fustet contains a peculiar colouring matter termed fustine, and in addition large quantities of tannic acid. It would appear that fustin yields quercetine by being split up in chemical sense.

Annatto, or Arnotto Is a yellow-red pigment, chiefly used for dyeing silk. It is met with in commerce as a thick paste of the consistence of putty, and is prepared in America, the West and East Indies, from the pulp of the fruit of the *Bixa Orellana.* According to Chevreul, annatto contains two different pigments; one of these exhibits a yellow colour and is soluble in alcohol and water, while the other, a red-coloured matter, is readily soluble in alcohol but not in water. Piccard states that the formula of the latter is $C_5H_6O_4$. Annatto is soluble in weak caustic and carbonated alkaline solutions.

Yellow Berries, or simply Berries. This drug is the fruit of various kinds of shrubs which are known by the general name of the dyer's buckthorn, the *Rhamus infectorius*, *R. amygdalinus*, *R. saxatilis* of the botanists, grown in the Levant, Southern France, and Hungary. The size of these berries varies very much, two sizes being chiefly met with and distinguished in commerce, viz., the large bright olive-coloured full-sized, and the smaller shrivelled deep brown berry. The former are gathered before they are quite ripe, while the others have been left after full maturity for a considerable time on the twigs. These berries contain a fine golden-yellow pigment named chrysorhamnine and olive-yellow xanthorhamnine. According to Bolley the former is identical with quercetine. Berries are used in calico-printing, for the colouring of paper-pulp, and for the preparation of lake colours.

Turmeric Is the dried root of the *Curcuma longa* and *C. rotunda*, a plant growing in India and Java, belonging to the natural order of the *Scitamineæ*. The root is met with in egg-shaped tubers or flattened lumps, exhibiting a dirty yellow colour. The pigment contained is termed curcumine, $C_8H_{10}O_2$. As a dye turmeric is chiefly used in silk-printing and dyeing, also for woollen fabrics for dark and full shades of colour. Upon cotton it dyes without mordant, but the colour is very fugitive. Turmeric test-paper is used for the detection of alkalies and boracic acid, by which it is turned red-brown.

Weld. This dye material consists of the dried herb and stems of a plant botanically known as *Reseda luteola*, a native of the southern parts of Europe and frequently cultivated for the use of dyers. French weld is considered the best. The pigment it contains is known as luteoline.

Quercitron Bark. This dye material, as its name indicates, is the inner bark of the black oak, *Quercus tinctoria*. It is a native tree of North America, and the drug is imported in the state of powder. The colour of this substance is bright yellow, and it contains tannic acid in addition to a yellow pigment, quercitrine, $C_{33}H_{30}O_{17}$. When quercitrine is treated with dilute acids it is split up, yielding quercetine, $C_{27}H_{18}O_{12}$, a lemon-yellow powder met with in commerce under the name of flavine. According to Hlasiwetz's opinion, quercetine contains the complex of morine. Owing to the beauty of the colour it yields, quercitron bark is, with picric acid, the chief yellow dye of the present day. Among the more or less important yellow dyes, we mention:—Saw-wort, *Serratula tinctoria*; dyer's brown, or greenwood, *Genista tinctoria*; the wongshy, Chinese annatto, or yellow pods, the seed capsules of the fruit of *Gardenia florida*, a plant belonging to the family of the *Rubiaceæ*; purrhee, or Indian yellow, *Jaune Indien*, a dye material imported from India, the origin of which is not known (it is the magnesia salt of purreic or euxanthic acid, and is stated to be obtained from the urine of camels); Morinda yellow, from the *Morinda citrifolia*. Since the tar-colour industry has sprung up, picric acid (see p. 580) is frequently used as a yellow dye, and mixed with either indigo or aniline blue, as a green dye for silk and woollen fabrics. In order fully to exhaust the picric acid dye-beck, some sulphuric acid should be added to it. More recently the so-called Manchester yellow (see p. 582) is frequently employed instead of picric acid. The latter is not used upon cotton.

Brown, Green, and Black Dyes. Brown dyes, aniline brown excepted, are mixtures of red, yellow, and blue, or of yellow or red with black. Frequently a brown is dyed by the use of oxidising agents with tannin-containing pigments, such as willow, oak, or walnut barks with cutch, the extract of the wood of the *Areca* and *Acacia catechu*, &c. The latter is technically termed chemick brown. Manganese, or bister brown, is obtained from the hydrated oxide of manganese. Black is obtained from tannate or gallate of protoperoxide of iron or from logwood decoction and chromate of potash[*] or from aniline black (see p. 579). Green is produced by mixing yellow and blue, or by the use of the Chinese green Lo-kao, obtained from *Rhamnus chlorophorus* and *R. utilis;* or by the use of sap-green from the berries of the *Rhamnus catharticus;* finally, aniline-green (aldehyde green and iodine green, see p. 578) is used, and yields a most beautiful dye.

BLEACHING.

Bleaching. The operation of bleaching aims at more or less perfectly whitening or decolourising the yarns spun from flax, hemp, jute, cotton, or of the textile fabrics woven from the same. Vegetable fibre resists the action of most chemical agents in use in the bleaching, while the foreign or incrustating or colouring matters, occurring chiefly on the surface of the fibre, are rendered soluble or completely destroyed. The bleaching of the fabrics and fibres which, such as linen or cotton tissues, consist mainly of cellulose, is based on this principle. The method of bleaching wool and silk differs from that of the vegetable fibres, inasmuch as the chemicals used for the latter would exert upon the former a solvent action, not only as regards the impurities, but the substance itself.

In the operation of bleaching, partly chemical and partly mechanical means are employed. On the large scale, setting aside all theoretical considerations which do not fall within the scope of this work, the operation of bleaching cotton fabrics consists of the following operations:—

1. Singeing, followed by "rot steep" or "wetting-out steep."
2. Liming—boiling with milk of lime and water for 12 to 16 hours.
3. Washing out the lime and passing in hydrochloric acid "sours" or weak vitriol.
4. Bowking in soda-ash and prepared resin, 10 to 16 hours.
5. Washing out the bowk.

[*] Ordinary black ink which, if really made with galls, consists essentially of gallate of protoperoxide of iron kept in suspension in water by the aid of gum arabic, is indeed a dye liquor. A very good black ink may be made as follows:—1 kilo. of coarsely pulverised nut galls and 150 grms. of logwood chips are exhausted with 5 litres of hot water; 600 grms. of gum arabic are dissolved in 2½ litres of water; and 500 grms. of sulphate of iron in some litres of water; each of these solutions being made separately. This done the gall-logwood infusion is mixed with those of the gum and copperas; a few drops of essential oil of cloves or of gaultheria (winter green oil) having been added, there is added as much water as will bring the bulk of the liquid up to 11 litres. While this kind of ink attacks and corrodes steel pens, it has the additional disadvantage that after a time the writing becomes yellow. In 1848 Runge called attention to an ink originally invented by Leykauf at Nürenberg, and improved upon by C. Erdmann at Leipzig and sold by him. This ink is made up of 1000 parts of a logwood decoction (1 part of wood to 8 parts of water) and 1 part of yellow chromate of potash, some bichloride of mercury being added for the purpose of preventing the formation of mould. This ink is cheap and very permanent; the colouring principle is a combination of hæmateine and oxide of chromium. Leonhard's so-called alizarine ink is made by exhausting with water, so that 120 parts of fluid are obtained from 42 parts of galls and 3 of madder. To this mixture is added 1·2 parts of sulphindigotic acid, 5·2 parts of green copperas, and 2 parts of pyrolignite of iron solution. Rouen's blue ink, frequently used in France, consists of a decoction of 750 grms. of logwood, 35 grms. of alum, 31 grms. of gum arabic in 5 to 6 litres of water. For an excellent extemporaneous ink, see "Chemical News," vol. xxv., p. 45. Copying inks are only more concentrated ordinary inks, to which more gum and sugar are added. Marking ink for linen is a solution of silver (see p. 105), or aniline black produced on the woven fabric (see p. 579).

6. Passing through a solution of chloride of lime (hypochlorite of lime).
7. Passing through weak hydrochloric acid.
8. Washing, squeezing, and drying.

The singeing is not a part of the bleaching process properly considered; its purpose is to remove the loosely adhering filaments, and improve the appearance of the cloth if required for printing.

The "rot steep" (so-called because the flour or size with which the goods were impregnated was formerly allowed to enter into fermentation and putrefaction) is intended to thoroughly saturate the cloth. The liming takes place in kiers or kettles capable of holding from 500 to 1500 pieces of cloth. The lime is very carefully slaked and brought to a smooth milk of lime, being sifted so that no small lumps of quick-lime shall get into the kier. The lime is equally distributed upon the cloth as it enters the kier. The cloth is pressed into the liquor and the boiling commenced and continued for a period of 12 to 16 hours. At the end of that time the liquor is run off and clear water run in to cool the pieces of cloth, which are then taken out and washed. The utility of the liming consists in its action upon the greasy matters, forming with them a kind of insoluble soap, which is easily removed by the subsequent processes. The souring after liming removes all excess of lime and breaks up the insoluble lime-soap, leaving the greasy matters upon the cloth, but in such an altered state as to be easily dissolved in the bowking which follows. Hydrochloric acid is sometimes used in this souring, but more commonly dilute sulphuric acid is employed. The bowking or boiling with alkali and soap has for its object the removal of the greasy matters; it dissolves them, and all the dirt held by them now comes out of the cloth, leaving the cotton nearly pure. The alkali used in this process is soda-ash. The soap is made from resin and called prepared resin. The last process is that of passing the goods through a clear solution of bleaching-powder for the purpose of destroying the slight tinge of colour of a buff or cream shade still adhering to the cotton. The solution of bleaching-powder is very weak, so that probably a piece of calico of the ordinary size does not take up more than the soluble matter from ¼ of an ounce of bleaching-powder. The goods are allowed to remain some time in soaking with the chloride of lime solution, and are next passed through sours for the final operation. The dilute hydrochloric acid has the effect of setting the chlorine free from the bleaching-powder and thus completing the destruction of the colour. At the same time it removes the lime and likewise any traces of iron (iron moulds) that may exist in the cloth. Linen is not so easily bleached as cotton, and it appears to suffer considerably by boiling with lime and by contact with bleaching-powder. It is, therefore, generally bleached by continual boilings with alkali and a few sourings with bleaching-powder; or as lime is injurious, the hypochlorites of potash or soda are substituted. Woollen goods or yarns are bleached by treating them with very mild alkaline liquors, which remove the fatty matters, lant and soap with soda crystals being the substances usually employed. Sulphurous acid gas—or, as it is termed in the trade, vapour of burning brimstone—is used to finish wool, giving it whiteness and lustre. The following is an outline of the process as described by Persoz for bleaching woollen goods; it is for 40 pieces each 50 yards long:—1. Passed three times through a solution of 25 lbs. of carbonate of soda and 7 lbs. of soap at a temperature of 100° F.; add ¾ lb. of soap after every four pieces. 2. Wash twice in warm water. 3. Passed three times through a solution of 25 lbs. of carbonate of soda at 120° F., and add ¾ lb. of soap again after every four pieces. 4. Sulphured in a room for twelve hours, using 25 lbs. of sulphur for the forty pieces. 5. Passed three times through a solution of soda, as in No. 3. 6. Sulphured again, as in No. 4. 7. Soda liquor again, as in No. 3. 8. Washed twice through warm water. 9. Sulphured a third time as in No. 4. 10. Washed twice in warm and then in cold water. 11. Blued with extract of indigo (indigo-carmine) according to taste.

Bleaching of Silk. The operation of bleaching silk is always preceded by removing (decorticating, degumming) the gummy substance attached to and externally covering the fibre. This is effected by boiling the raw silk in soap and water. For the purpose of bleaching silk nothing but water, soap, and sulphur (for making sulphurous acid) are used. Occasionally some soda crystals are employed to save soap but as alkalies injure, and if incautiously used destroy, the fibre, they must be employed with extreme care. Bran is sometimes used with soap in order to neutralise any excess of alkali (bran contains, or rather develops, when it becomes wet, lactic acid). The process is terminated by passing in an extremely diluted sour (solution of sulphuric acid in water) so weak as scarcely to be acid to the taste. Sulphuring is only required for silks intended to be left either white or to be dyed or printed with bright and light colours. This operation requires great care and should be seldom resorted to.

This is an outline of the process of bleaching as carried on in practice on the large scale in this as well as in other countries. The theoretical consideration of the mode of action of the substances employed belongs to theoretical chemistry, and is treated under the heads of Chlorine, Sulphurous Acid, Oxidising Substances, &c.; and as far as the textile fibres are concerned, under Cellulose for flax, hemp, jute, cotton, and the Animal Fibres for wool and silk. The meadow bleaching of cotton and linen fabrics is still resorted to in some extent, but only in connection with the processes already referred to. None of the novelties proposed for bleaching purposes—among these, for instance, the use of permanganate of potash (Tessié du Motay's process) as a bleaching agent—have been found by practical bleachers of great experience to be either better, more manageable, or cheaper than the methods sanctioned by lengthy experience and daily use.

Dyeing of Spun Yarn and Woven Textile Fabrics.

Dyeing. Just as animal charcoal and arable soil are possessed of the property to assimilate in their pores colouring matter and some inorganic substances without the latter being altered, so also do animal and vegetable fibres possess the property of absorbing from solutions, and fixing in a more or less insoluble condition, dyes and some of the constituents of mordants. This combination, or more correctly union, is often so loose that it is readily broken up by repeated treatment with solvents (viz. simply washing with water or soapsuds), especially if aided by heat. Thus, for instance, a textile fibre dyed (rather tinged, for dyeing implies fixity) with sulphindigotic acid, or a solution of Berlin blue in oxalic acid, may be decolourised again by repeated washing in water. A fibre can only be called dyed in the strict sense when the dissolved dye material has been united in *insoluble* condition with the fibre, for which purpose often the intervention of a third substance, viz., a *mordant*, is required, the union thus formed resisting the action of solvents, that is to say—repeated washing with warm water and soap. The colour thus produced is termed fast, and resists the action of light, air, soap-water, weak alkaline solutions, and weak acids. A dye which does not resist these agents is termed fugitive. Dyeing is partly based on chemical principles, but as regards the taking up or fixing of the dye by the fibre, it would appear to be only a physical attraction, capillarity, as there does not exist between a certain quantity of fibre and of dye an atomistic relation. Moreover, neither fibre nor dye have lost, after fixation has taken place, their characteristic properties.

The insoluble condition of the union between fibre and dye may be obtained in various ways, viz.—1. By removal of the solvent, as, for instance, oxide of copper dissolved in ammonia may be fixed on the fibre by simply evaporating the latter fluid; chromate of zinc dissolved in ammonia may be fixed in the same manner. The precipitation of carthamine from its alkaline solution by the aid of an acid, and the precipitation of some of the tar colours from their alcoholic solutions belong to the same category. The insoluble condition can be produced by—2. Oxidation, the previously soluble dye being rendered insoluble by taking up oxygen (ageing process).

The ferrous and manganous sulphates becoming converted by oxidation into insoluble hydrated oxides; and further, those dyes of vegetable origin which, in addition to tannic acid, also contain a peculiar dye material, such as quercitron, sumac, yellow-wood, fustet, &c., belong to this category. When any textile fabric is impregnated with an aqueous or alkaline infusion of these substances, and then aged or stoved (technical terms for exposure to action of air in what are termed ageing-rooms), the dye material becomes brown, and is then no longer soluble in water. This is more rapidly effected by treating the textile fabrics, previously impregnated with the solutions of the drugs, with oxidising substances—for instance, chromic acid or bichromate of potash. Another instance of this kind is the process of dyeing black with logwood and chromate of potash, whereby the hæmatoxyline of the wood is oxidised, and the chromic acid reduced to chromic oxide. To some extent the dyeing blue with indigo in the vat (blue vat), to be more fully described presently, belongs to the same category; but in this case the production of the colour is due to the gradual absorption of oxygen, while simultaneously hydrogen is evolved from the white indigo, the hydogen combining with oxygen and forming water. The formation of aniline black upon tissues by the aid of ozone-forming substances (chlorate of potash, ferricyanide of ammonium, chromate of copper, freshly precipitated sulphide of copper) belongs to this class. In many cases the insoluble condition (3) is obtained by double decomposition; as, for instance, blue is produced by hydroferrocyanic acid and oxide of iron; green by arsenite and sulphate of copper; yellow by chromate of potash and a soluble lead salt. This mode of fixation of pigments is only employed with mineral colours. The most important and most ordinary method of fixing dyes is (4) by the aid of mordants. We understand by a mordant, a solution of some substance which, not being itself a dye, has an affinity as well for the fibre as for the dye material, and is thereby capable of effecting the fixation of the latter to the fibre.

The more important mordants are:—Alum; sulphate, acetate and hyposulphite of alumina; aluminate of soda; and acetate of iron; according to Reimann [1870], amorphous silica may be used for fixing several dye materials; tin mordants; fatty substances, Gallipoli oil, in Turkey-red dyeing; tannic acid, for madder colours; cochineal colours; aniline dyes on cotton and linen fabrics; albumen, dried white of egg, gluten, caseine, and fatty oils (linseed oil also sometimes). The fabrics to be dyed are impregnated with the mordants, which are next fixed, an operation differing according to the nature of the mordant as well as the specific dye it is required for; but in general terms, ageing, dung-bath, bran-bath, and soaping, are employed, after which the woven fabric is placed in the dye solution contained in the dye-beck. Most of the dyes of organic origin can be fixed only by the aid of mordants.

Mordants.

Bancroft considers dyes as substantive and adjective. By the former is understood those which without the aid of a mordant become fixed upon the textile fibres in an insoluble condition: to these belong all mineral pigments; and among the vegetable colouring substances—indigo, turmeric, annatto, safflower, also most of the tar-colours, although, as already mentioned, tannic acid is used for fixing fuchsin and similar tar-colours. By adjective colours or dyes is understood such as require an intermediate substance (a mordant in fact) to become fixed upon the fibre in an insoluble condition. These intermediate substances are termed mordants; they not only serve for fixing the dye to the textile fibres, but also produce in the mordanted goods such an alteration that the parts of the tissue where the composition is applied appear white when the goods are taken from the dye-beck. The substances which produce this effect are technically termed dischargers, or discharge compositions; among them are phosphoric, tartaric, oxalic, arsenious acids, &c.; but in practice the goods are first uniformly dyed, and the discharge then applied so as to act only where it is desired to exhibit a pattern. What are termed resists are not mordants, but only compositions applied to the woven fabric at certain parts where it is desired that no deposition of colour or mordant shall take place. Mordants may modify the original colour that a dye yields; as, for instance, with alumina compounds madder yields red, pink, and scarlet; with salts of iron, according to the degree of concentration, lilac, purple, black; and brown with certain salts of copper. For the purpose of clearing and brightening (*avivage*), the dyed or printed goods are passed through solutions of either dilute acids, weak or strong alkalies, soap-suds, bran-bath, solutions of bleaching-powder, or also of some other dye material.

Dyeing Woollen Fabrics. Wool is sometimes dyed in the flock or fleece, that is to say, when not spun; sometimes in yarn or worsted and as a finished woven fabric (cloth, broadcloth, &c.). As there is always some refuse wool in the operations of weaving, fulling, and dressing the woollen tissues, it is advantageous to dye wool in the condition of spun yarn. When the dye intended to be applied to wool is fast, the textile fibre is first mordanted. For this purpose the woollen fibre is treated with a solution of alum and cream of tartar (bitartrate of potash); or with the latter salt and tin-salt (chloride of tin); or, again, cream of tartar and green vitriol; for certain colours, chloride of tin and pink salt (see p. 75) are used.

Dyeing Wool Blue. The imparting of a blue colour to wool is one of the most important operations of dyeing woollen goods. It is frequently effected with indigo, which produces the most beautiful and fast colours; but indigo is used only for the better and heavier kinds of woollen fabrics; lighter tissues—merinos for instance—are often dyed with Prussian blue (not a fast colour), while common woollen goods, flannels, &c., if dyed blue at all, are dyed with logwood and blue vitriol (sulphate of copper). In order to ascertain whether a woollen tissue has been dyed with indigo, Prussian blue, or copper salts, the following tests may be employed. Woollen tissue dyed with indigo does not change its colour by being boiled with caustic potash, or by being moistened with concentrated sulphuric acid. When Prussian blue is the dye used, the tissue becomes red-coloured by being boiled with caustic potash, and becomes discoloured by being moistened with strong sulphuric acid. Woollen goods dyed with logwood and copper salts are reddened by being moistened with dilute sulphuric acid, and on being incinerated, the tissue leaves an ash containing copper.

Indigo Blue. Woollen goods are most frequently dyed blue with indigo by means of a solution of white indigo (reduced indigo) in an alkaline fluid, the goods being blued by exposure to air—that is to say, by the oxidation of the indigo taken up by the fibre, the dye becoming simultaneously fixed. The principle of this mode of dyeing with indigo (technically known as blue vat), may be elucidated by the following formula:—

$$C_{16}H_{12}N_2O_2+O=C_{16}H_{10}N_2O_2+H_2O.$$

Blue Vats. The greatest consumption of indigo is in forming the blue vats, in which woollen or cotton goods, more rarely linen, are dyed by simply immersing them in the solution of white indigo. The same vats are not equally adapted for wool and calico, there being, as will be seen in the following details, a wide difference in their composition. According to the general accounts, the lime and copperas vat (see below) is not well adapted for woollen goods; still in the most recently published French treatise on woollen dyeing, there is no mention made of any other kind of vat; the following proportions and directions being given for setting a vat for dark blue:—1200 gallons of water; 34 lbs. of quick-lime; 22 lbs. of green copperas; 12 lbs. of ground indigo; 4 quarts of caustic potash solution at 34° = sp. gr. 1·288. The indigo is ground very fine by trituration in properly constructed mills, this being a point of the utmost importance. In the above recipe the potash is mixed with 5 gallons of water in an iron pan, and the indigo added. The mixture is gradually heated to ebullition and kept boiling for two hours with uninterrupted stirring; this softens and prepares the indigo for dissolving. The lime is well slaked so as to be very fine, and is next passed through a sieve in the state of milk of lime. It is then mixed with the indigo and potash; the copperas (protosulphate of iron), previously dissolved, is added to the vat and well stirred; then the mixture of lime, potash, and indigo is poured in, and the whole well stirred for half an hour. If the proportions are well kept, the vat will be fit for working in twelve hours; if, however, it looks blue under the scum, it is a sign that the indigo is not wholly dissolved, and more lime and copperas should be added, and the vat left undisturbed for another twelve hours. The vat is worked at a temperature of 70° to 80° F. This is the ordinary composition of a vat for dyeing cotton, but is not, at least in England, in use for dyeing woollen goods.

The usual blue vats for wool contain neither copperas nor lime, or but a small quantity of the latter; as, for instance—Water, 500 gallons; indigo, 20 lbs.; potash (carbonate, pearl-ash), 30 lbs.; bran, 9 lbs.; madder, 9 lbs. The water is heated to just below its boiling-point; the potash, bran, and madder are first put into the vat, a well-made wooden tub of convenient size, and then the indigo previously very finely ground. Cold water is added so as to reduce the temperature to 90° F., and that temperature is maintained constantly by means of a steam-pipe. The ingredients are well stirred every twelve hours. The vat is generally ready for use in forty-eight hours after setting. This vat does not work longer than about a month, and is somewhat expensive on account of the potash. Another—the so-called German—vat is much more manageable, and may be worked for two years without emptying, being freshened up as required. It is composed of the following ingredients:—2000 gallons of water are heated to 130° F., and there are added

20 lbs. of crystals of soda (common carbonate); 2½ pecks of bran; and 12 lbs. of indigo; the mixture being well stirred. In twelve hours fermentation sets in; bubbles of gas rise; the liquid has a sweet smell, and has assumed a green colour. 2 lbs. of slaked lime are now added and well stirred, the vat is again heated and covered up for twelve hours, when a similar quantity of bran, indigo, and soda, with some lime, are added. In about forty-eight hours the vat may be worked; but as the reducing powers of the bran are somewhat feeble, an addition of 6 pounds of molasses is made. If the fermentation becomes too active, it is repressed by the addition of lime; if too sluggish, it is stimulated by the addition of bran and molasses. Like all the other blue vats for wool it is worked hot. Another kind of vat may be called the woad vat, because a considerable quantity of woad is added to it, and also madder, which in this case acts simply by reason of the saccharine matter it contains. The proportions are:—Pulverised indigo, 1 lb.; madder, 4 lbs.; slaked lime, 7 lbs., boiled together with water and poured upon the woad in the vat. After a few hours fermentation sets in, and fresh indigo is added according to the depth of colour required to be dyed. The pastel vat is set with a variety of woad which grows in France, and which is richer in colouring matter than the common woad. It is possible that the colouring matter of the pastel adds to the effect; but it is more likely that while it furnishes fermentescible matters useful in promoting the solution of indigo, it is added as a remnant of ancient usage. Before indigo became again known in Europe (the dye was known to the Greeks and Romans), in the 17th century, woad was the general blue dye material. The method of dyeing the woollen fibre and fabrics is very simple. The wool, thoroughly wetted out, is suspended on frames, and dipped in the vat for an hour and a half or two hours, being agitated all the time to insure regularity of colouring. The pieces are then removed, washed in water, and treated with weak hydrochloric or sulphuric acids to remove the alkali retained. As regards blue vat for cotton dyeing, in some exceptional cases when thick and heavy goods have to be dyed, the so-called German vat is used; but generally all calicos are dyed blue by means of the cold lime and copperas vat. The materials used are lime, protosulphate of iron, ground indigo, and water. The chemical action consists, in the first instance, in the formation of sulphate of lime and protoxide of iron; the latter substance having a considerable affinity for oxygen, removes an atom of it from the blue indigo, converting it into white, which dissolves in the excess of lime, and is ready for dyeing. The proportions are as follows:—900 gallons of water; 60 lbs. of green copperas; 36 lbs. of ground indigo; 80 to 90 lbs. of slaked lime, stirred every half hour for three or four hours, then left twelve hours to settle, well raked up again, and as soon as settled ready for dyeing.

Saxony Blue. As already stated, indigo dissolves in concentrated sulphuric acid, forming (because it is not a solution in the ordinary sense of the word) sulphindigotic acid, which is employed in dyeing wool in the following manner:—First, 1 part of indigo is treated with 4 to 5 parts of fuming sulphuric acid; next, this solution is poured into a vessel containing water; and into this mixture flock wool is immersed for twenty-four hours. After this time the wool is removed from the vessel and drained, and transferred to a cauldron filled with water, to which has been added either carbonate of ammonia, or of soda, or of potash, and boiled for some time. The solution thus obtained, technically known as extract of indigo or as indigo carmine, is used for dyeing wool which has been previously mordanted with alum. There is formed on the wool sulphindigotate of alumina.

Recovering Indigo from Rags, &c. In order to recover the indigo from scraps and rags of woollen and other fabrics dyed indigo blue, the materials are treated with dilute sulphuric acid, which is heated to 100°. The wool is dissolved, while the indigo is left as an insoluble sediment. Military uniforms yield from 2 to 3 per cent of indigo. The acid solution is next neutralised with chalk, and a sulphate of lime is obtained which, owing to the nitrogenous matter intermingled, may be usefully employed as a manure.

Berlin or Prussian Blue on Wool. Wool is dyed with the so-called Prussian blue (ferrocyanide of iron) by two methods, one of which consists in saturating the wool with a solution of a salt of peroxide of iron (generally the persulphate, or preferably the pernitrate), after which the wool is passed through a solution of ferrocyanide of potassium in water, acidulated with sulphuric acid. The other process producing so-called *Bleu de France* is based upon the decomposing action which the atmosphere exerts on the ferro- and ferri-cyanhydric acids. The goods are immersed in a solution of either the ferro- (yellow) or ferri- (ruby red) cyanide of potassium (commonly yellow or red prussiate) in water, to which are added sulphuric acid and alum. Afterwards the goods are aged, or exposed to the air in rooms in which steam is simultaneously admitted to elevate the temperature and assist the action of the oxygen of the air. The result is that the ferro- or ferri- cyanhydric acid is decomposed, hydrocyanic acid being evolved, while there is deposited on the fibres of the woven fabric ferrocyanide of iron, Prussian or Berlin blue. Meitzendorff has recently invented a method of dyeing this blue by which a colour is produced very similar to that obtained by the so-called Saxony blue. He prepares a solution containing ferrocyanide of potassium, chloride of tin ($SnCl_4$), tartaric and oxalic acids; this solution is heated and the wool kept therein for some time. The oxalic acid dissolves the Prussian blue, which of course can only act as a dye when dissolved, any of it left undissolved being lost. The tartaric acid increases the brilliancy of the colour.

Dyeing Blue with Logwood and a Copper Salt. For this purpose logwood is boiled in the dye-beck with water, and to the decoction are added alum, cream of tartar, and sulphate of copper. The wool is boiled in this fluid, and is next cleared by being boiled in a fluid containing logwood, tinsalt (protochloride of tin), alum, and cream of tartar. The goods dyed in this manner do not, as is the case with the indigo goods, become white by wear. Instead of logwood, archil and cudbear are frequently used for so-called half-fast colours.

Dyeing Yellow. On the Continent, weld, which has become quite obsolete for dyeing yellow on wool in the United Kingdom, having been entirely superseded by quercitron bark, is still used for producing a yellow dye, on account of the fact that weld, when brought into contact with an alkali, becomes less red-coloured than is the case with the other yellow dyes.

In dyeing with weld its colouring matter is extracted by water, and the decoction added to the goods intended to be dyed. With alum it dyes a very fine clear yellow, tolerably permanent in soap, but not resisting air and light. Weld has not more than one-fourth the tinctorial power of quercitron bark, and on this account, as well as on that of its great bulk relative to its weight, it is not used in this country. Fustic, yellow-wood, is very extensively employed in dyeing, and is the most suitable yellow matter for working with other colours in compound shades. With aluminous mordants it gives yellow of an orange shade; with iron mordants it gives drabs.

greys, and olive. As a yellow colouring matter it is considered to be of far less power than quercitron bark weight for weight, while it is also inferior in purity of colour; but as fustic withstands the action of acids and acid salts better than bark, it is used in greens, blacks, and mixed colours where yellow is required. Young or French fustic (also known as *Venice sumac*) is used for imparting yellow to merinos. A golden yellow is produced upon wool with either picric acid or Manchester yellow.

Dyeing Wool Red. Madder is the chief colouring matter employed for imparting to wool a red or scarlet colour. The process of dyeing wool with madder consists in mordanting the woollen tissue, fibre, or yarn, and in immersing it in the dye-beck containing madder with water. The wool is mordanted by being immersed in a warm solution of alum and cream of tartar. The dyeing is effected by placing the mordanted goods in the dye-beck or madder-bath, the quantity of madder being equal to half the weight of the woollen goods. In practice the goods are, of course, slowly moved into, through, and out of the dye-beck, proper mechanism being provided for this purpose. After having been dyed, the goods are thoroughly washed, so as to remove excess of dye as well as any mechanically adhering particles of madder. Dyeing red with cochineal is effected upon wool in the same manner as with madder. Scarlet is red with a yellowish hue, while a peculiar hue of red is termed crimson, often produced by cochineal. Woollen fabrics are mordanted in a mixture of water, cochineal, cream of tartar, and tinsalt, and next dyed by boiling with more cochineal and tinsalt. Wool is very readily dyed with all the tar-colours (red, blue, green, grey, yellow, brown, violet), the affinity of wool for these colours being so great, that the solution of any of these pigments may be completely deprived of its colouring matter by contact with wool.

Green Dyes. Green dyes are usually obtained by combining blue and yellow. Wool is first dyed blue, and having then been mordanted with cream of tartar and alum, is dyed with fustic, or, on the Continent, with weld. The green cloth used for covering billiard-tables and other furniture is dyed in the following manner:—A weak decoction of fustic is prepared, and into this some Saxony blue is poured, while there is next added alum and cream of tartar. The woollen fabric is immersed in the bath and boiled for two hours. It is next thoroughly washed and brightened by being again immersed in a dye-beck filled with a fresh fustic decoction, to which a smaller quantity of Saxony blue has been added. All kinds of woollen tissues, worsted, half-wool, alpacas, delaines, &c., may be dyed green by means of lo-kao (Chinese green), and iodine green.

Mixed Shades. Mixed shades are produced on the fabrics by means of cochineal, madder, French fustic, fustic, in a manner similar to that used for dyeing green.

Black Dyes. Excepting only aniline black, all black dyes may be considered as combinations of iron with tannic or gallic acid; but the best and fastest blacks on broadcloth are such as have as a first dye either madder or indigo. The woollen goods are mordanted with sulphate of iron (green copperas) and dyed by immersion in a decoction of logwood, galls, sumac, &c. The so-called Sédan black (this town is celebrated for its cloth manufacture) is produced by dyeing the cloth blue with woad, when after careful washing the cloth is placed in a dye-beck containing water, sumac, and logwood, and is boiled for some three hours, after which sulphate of iron in a solution of known strength is added. This operation is repeated until the cloth has assumed an intensely black colour. Half-fast black colours are produced on cloth by dyeing them blue with Prussian blue, after which the operation just described is gone through. Common black is produced by dyeing with logwood, sumac, some fustic, and a mixture of green and blue vitriol. Chromium black, invented by Leykauf at Nüremberg, is obtained in the following manner:—The cloth is mordanted with a solution of bichromate of potash and cream of tartar, after which it is dyed in a decoction of logwood. The so-called pyrolignite of iron (crude acetate of iron prepared from scraps of old iron and crude acetic acid) is now very generally used as a mordant instead of the green copperas. This acetate, also known as black or iron liquor, is prepared on the large scale and sold as a liquid at a sp. gr. of 1·09 to 1·14.

White Cloth. This cloth, in use especially for military uniforms, is obtained by first thoroughly washing, fulling, and carefully sulphuring the cloth, which is next passed through a bath containing chalk and a small quantity of size, after which it is dried, beaten, and well brushed.

Silk Dyeing. Silk is usually dyed in skeins unspun, but having been first decorticated, that is to say, deprived of the layer of gummy matter which forms the outer covering of cocoon silk. It is then scoured, bleached, and sulphured; the latter only when the silk is to be dyed with very bright colours and delicate light hues. Silk is dyed in cold dye solutions. It is dyed black by any of the following processes:—

1. Logwood and iron mordant;
2. Logwood and bichromate of potash;
3. Galls and other substances containing tannic acid with iron salts as mordant;
4. With aniline black, according to the recipes of Persoz, jun., and others, by the use of chromate of copper and oxalate of aniline.

The first and second are simply known as ordinary blacks, while the third is known as fast black. The ordinary black is obtained by simply mordanting the silk with nitrate of iron, and then dyeing it in a decoction of logwood. This cheap dye is more particularly applied to light silken fabrics. The colour is reddened even by weak acids, such as lemon and orange and other fruit juices. The fast black is far more expensive, but it is not affected by weak acids, while it affords the additional advantage of largely increasing the weight of the silk (in raw state as well as in spun-yarn silk is sold and bought by weight), as this textile fibre absorbs from 60 to 80, and even 100 times its own weight, and silk used for shoe-laces even 225 per cent of the dye material. When desired the silk-dyer has to return for 100 lbs. of raw silk from 160 to 180 or 200 lbs. weighted black-dyed silk. In Germany an indigenous gall, locally known as *Knoppern*, *French avèlandes*, containing some 30 to 50 per cent of tannic acid, is used in the extract to dye silk black. In England nut-galls imported from the Levant are employed for this purpose. Although the increase in weight of the silk by black dyeing is advantageous to the dealers, the deposition of so much foreign matter in the fibre of the silk not only injures its wearing qualities, but also gives rise to the disagreeableness of the dyeing coming off while the material is being worn. Microscopic research has proved that the dye adheres very loosely to the silk. The process of dyeing silk black with galls is very simple. The fibre is first steeped in a solution, or rather infusio-decoction, of galls, technically known as "galling," after which the silk is placed in a solution of nitrate of iron. This black is sometimes dyed on silk previously dyed with Prussian blue, but far more frequently a bluish shade is given to black by first dyeing the silk with logwood, copperas, and some sulphate of copper.

As regards the weighting of the silk, it is essentially due to the fact that silk, as an animal product, has the property of combining with tannic acid and thereby becoming heavier. The larger, therefore, the quantity of tannic acid contained in the dye-bath, or the oftener the galling of the silk is repeated, the heavier the fibre will become within certain limits. It is not quite indifferent whether a per-salt or a proto-salt of iron be employed, the former being preferable. The previously galled silk becomes, when passed through a solution of a per-salt of iron, at once coloured black; but when it is passed through a solution of a proto-salt of the same metal, the silk becomes at first coloured only black-violet, and gradually deep black by exposure to air. Although in every case the result is the same, the use of a per-salt is advantageous, and becomes necessary with a small quantity of tannic acid, while for a heavy weighting of the silk, the proto-salt of iron only can be employed. It is stated that the dyeing of silk with aniline black by means of chromate of copper and oxalate of aniline yields excellent results. Silk is dyed blue either with indigo, Berlin blue, ogwood, or aniline blue. The indigo vat has not been much used for imparting a blue colour to silk since the discovery of fixing Prussian blue upon silk; and if indigo is used at all it is as indigo carmine, or the so-called distilled blue, purified sulphindigotic acid. In order to dye silk with Prussian blue, it is first immersed in a solution of nitrate of iron. This salt is generally in use in England, while in France a persulphate of iron made by dissolving green copperas in nitric acid is employed, and known under the name of Raymond's solution, the blue produced being termed Raymond's blue; Napoleon blue is produced by the addition of a tinsalt to the iron bath, followed by treatment with a solution of ferrocyanide of potassium acidulated with sulphuric acid. The latter blue, more brilliant than the former, is usually prepared in England, a tinsalt being invariably added to the iron mordant. The mordanted silk is next passed through a boiling soap-solution, then washed, and next steeped in a solution of ferrocyanide of potassium acidulated with hydrochloric acid. The brilliancy of the dyed silk is greatly enhanced by passing it through water containing ammonia. Dyeing silk with aniline or naphthaline blue is a very simple process, it being only necessary to put the silk into a solution of the dyes, the solvent being alcohol or wood-spirit, or in the case of soluble aniline blue, water. The silk is left in the solution until it has assumed the desired hue. Until the discovery of fuchsin, silk was always dyed red and pink by means of cochineal, safflower (carthamine), and archil; but now silk is generally dyed with fuchsin, coralline, and Magdala red (naphthaline red). The process is as simple as that just described for aniline blue. Aniline red is the brightest, purest, and deepest of all red dyes for silk, but it is not so fast as Magdala red. Archil is still largely used, but aniline violet or mauve is in close competition with it. Yellow is produced upon silk by first mordanting with alum and dyeing in a decoction of weld, to which, if it be desired to impart an orange hue, some annatto is added, or, preferably, Manchester yellow. By cautious treatment with nitric acid silk may be dyed yellow, some xanthroproteic acid being formed, while without any mordant picric acid produces a bright lemon-yellow on silk, the colour becoming deeper by treatment with alkalies. Ordinary green is produced upon silk by dyeing it yellow by means of either weld, quercitron, fustic, or picric acid, and then dyeing it blue with indigo-carmine, aniline blue, or sulphindigotic acid. Fast green is obtained by dyeing the silk blue with *Bleu Raymond*, and next treating it with fustic. During the last few years aniline green (emeraldine) has been generally used for dyeing silk green. Lilac is produced upon silk by means of aniline violet, archil, or logwood and tinsalt.

Calico Dyeing. Cotton is dyed either in yarn or woven fabric, but more generally as yarn. Cotton is far more difficult to dye than wool, and requires, especially for obtaining fast colours, stronger mordants. Blue is produced upon cotton (calico it is termed in fabric) by means of the copperas-vat (see Indigo); further by Berlin or Prussian blue, logwood, and green copperas; and finally by being passed through a solution of oxide of copper in ammonia; the fibre, yarn, or tissue exhibiting after drying a beautiful bright blue colour. Yellow is produced with Avignon berries, weld, fustic, quercitron, annatto, acetate of iron (nankeen), and chrome-yellow. Green is obtained by the copperas-vat followed by dyeing with fustic. Brown is produced with a salt of iron and with quercitron or madder, or simply by means of hydrated oxide of manganese. Black is either fast, aniline black, or is produced by dyeing blue by the aid of the copperas-vat, next mordanting with acetate of iron, and then dyeing in a bath consisting of galls and logwood. The aniline colours can be fixed upon cotton only by the aid of a specific mordant—a solution of tannin in alcohol; or the fibre of cotton is first *animalised*, as it is termed; that is to say, impregnated with either albumen or casein, the fibre being to a certain extent made similar to that of wool or silk and rendered absorbent of aniline dyes. Cotton may be mordanted with Gallipoli oil, or with soft-soap for certain dyes.

As regards dyeing cotton and calicos red, madder is the chief dye material, while probably at no distant period artificial alizarine from anthracen will become an important material. We distinguish between ordinary red and Turkey, sometimes termed Andrinople red; the former is produced upon cotton goods mordanted with acetate of alumina (commonly called red liquor or red mordant); the latter is obtained by complicated manipulation, the *rationale* of which is not quite elucidated by science.

Turkey Red. This beautiful and very fast red, improved by washing, is produced by the following distinct operations:—The well-bleached cotton goods are first padded in a mixture of Gallipoli oil and pearl-ash containing about 200 lbs. of oil, 40 lbs. of pearl-ash, and 100 gallons of water, a quantity sufficient for about 4000 yards of calico. The pieces are next exposed to air in summer and to the heat of a stove in cold weather for twenty-four hours; then padded again in a mixture of oil, potash, and water, and again dried and exposed, and so on for as many as eight different treatments for dark colours. The excess of oil, or rather that which has not suffered change by oxidation, and the alkali are now removed by steeping in an alkaline fluid, and the pieces well washed. The next process is the galling and aluming; 60 lbs. of ground nut-galls are exhausted with hot water, and to this liquor are next added 120 lbs. of alum and 10 lbs. of acetate of lead, after which the liquor is made up to 120 gallons. The pieces are padded in this liquor, dried, and aged three days, then fixed by passing in warm water containing ground chalk, being next washed and dyed in madder mixed with a little sumac and with blood. For dark shades of colour the fabrics undergo another galling and aluming after dyeing, and are then aged, fixed, and dyed a second time. After this last operation the goods exhibit a very heavy brown-red colour, and they are brightened by two or three soapings or a passage in dilute nitric acid. In other processes sheeps' and cows' dung are mixed with the oil and other modifications introduced. Garancine is largely used in Turkey-red dyeing. By its use the operations of clearing and brightening (*avivage*) have been much shortened. All that has been suggested as regards the *rationale* of the Turkey-red dyeing process, and more especially as regards the action of the Gallipoli oil (*huile tournante*, an inferior kind of olive oil which, when mixed with a weak solution of pearl-ash, should, if of proper quality, form a perfect emulsion, which, after twenty-four hours' standing, should not exhibit any globules of oil floating on the surface), is not sufficiently substantiated to afford a secure basis for further reasoning.

Dyeing Linen. Linen is dyed by processes similar to those in use for cotton, but owing to the peculiar structure of the flax fibre, its affinity for dyes is much lower than that of cotton.

THE PRINTING OF WOVEN FABRICS.

Printing of Woven Fabrics. This very important branch of the dyer's art aims at producing coloured patterns upon calico, linen, and woollen and silk tissues. Calico printing is the most important portion of this industry, which is based upon the same principles as dyeing, but is in the practical execution far more difficult, partly because the colours have to be applied to certain portions only of the fabric, while others either remain colourless or are discharged, partly also because it frequently happens that many colours have to be applied close to each other. The colours employed in calico printing are of two different kinds; first, such as are directly applied to the cloth by the aid of blocks or plates upon which the patterns and designs to be produced upon the calico are engraved—to the colours thus applicable belong, also, the ochres, Berlin blue, madder-lake, indigo, cochineal, and most of the tar colours; secondly, the other kind of colours are such as are produced by immersing the calico printed with various mordants in dye-baths—madder, cochineal, logwood, weld, sumac, cutch, &c., belong to this category.

There exist various methods of printing, of which the following are the chief:—

1. From the thickened and mordanted colours.
2. The thickened mordant only is applied by means of engraved copper cylinders to the cloth, which, after the mordant has been thoroughly fixed, is put into the dye-beck.
3. The entire piece of cloth is either mordanted or a colour is printed, while to such portions of the cloth as are to remain white or are intended to be afterwards of another colour or colours, or pattern, a resist is applied, sometimes printed from blocks, or more frequently from cylinders, the effect being that on the portions of the cloth thus protected the dye does not become fixed.
4. Coloured patterns may be, and in practice are, largely produced by first dyeing the mordanted cloth (calico nearly always requires a mordant) uniformly with one colour, and removing this colour in certain portions of the cloth by what are technically termed discharges, that is to say, chemicals which destroy the dye.

In order to fix certain kinds of colours they have to be submitted to the action of steam (steam colours); while such inorganic substances as ultramarine, emerald green, &c., or among the semi-organic, the lakes of madder for instance—which are applied mechanically by the aid of albumen, caseine, gluten, and also require for fixing the aid of steam—are technically termed surface-printed colours.

Mordants. The mordants employed in calico printing are chiefly such salts as are comparatively loose combinations of acid and base, so that the latter can readily unite with the fibre. Among the mordants chiefly used the acetates of alumina (see p. 263) and iron occupy a first place, while alum or a solution of aluminate of soda is more rarely used. Acetate of lead is the mordant for producing chromate of lead; various combinations of tin (see p. 75) are also employed as mordants. The application of a mixture of caseine and lime has been recently proposed as a mordant; for this purpose caseine, technically known in England as lactarine, and prepared from milk (of which it is the curd), is dissolved in dilute caustic ammonia, and the solution thus obtained is mixed with freshly prepared milk of lime. The caseine-lime mixture is used for steeping the cloth intended to be dyed; the caseine-lime becomes insoluble by the application of heat, after which the fabric is so thoroughly mordanted that it resists washing with alkaline fluids. In order to prevent the stiffness of the cloth when the caseine-lime is used as a mordant, it has been suggested to mix the fluid, previous to its application to the woven fabric, with some Gallipoli oil; the calicos to which this mordant is applied behave as regards the dyes like wool, and readily take the same colours. Cheese, which does not contain too much fat, or skim-milk cheese, when digested with ammonia, produces a solution which can be used instead of caseine. Tannic acid, albumen, dried white of eggs re-dissolved in water, and vegetable gluten are used as mordants in calico printing.

Thickenings. In order to give the colours or mordants used in printing, either by block or cylinder, a sufficient consistency, they are mixed with what are technically known as thickenings. As such are used:—Senegal gum, tragacanth, leiocome, British gum, dextrine, salep, flour, gluten, pipe-clay with gum, glue and size, sulphate of lead, sugar, molasses, glycerine, starch, sometimes chloride and nitrate of zinc. The purity of the colours and mordants depends in a great measure upon the quality of the thickenings. British gum, prepared from starch, is most frequently used. As regards the selection of the thickening, it should be borne in mind that very acid mordants cannot be mixed with starch, because it loses its consistency with acids; while again, some metallic preparations—for instance, basic or sub-acetate of lead, solutions of tin, nitrate of iron, and of copper—cause gum to coagulate, and hence gum should not be used as a thickening with these substances.

Resists, or Reserves. As already stated, there is used in calico printing a composition which, on being applied to the cloth, prevents the deposition or fixing of colour to the portions of the cloth where the resist composition is placed, the result being that these portions are left white. Most frequently the resist is employed with the view of preventing the fixation of indigo to certain portions of the cloth, so that it remains white where the resist has been applied. The resists are composed of pasty excipients, such as pipe-clay, fat, oil, sulphate of lead, to which are added and with which are incorporated substances which readily yield oxygen, for instance, sulphate, nitrate, and acetate of copper, or a mixture of red prussiate of potash (ferricyanide of potassium), and caustic soda solution. In some instances resists are composed so that they act as a mordant (alumina or iron mordants) for other dyes, the portions of the cloth protected by the resist from contact with indigo, and left white, being dyed by immersion in a dye-beck containing another dye-stuff, which may be madder or quercitron bark. This kind of printing is sometimes termed *lapis*, in consequence of the remote similarity which some of these patterns bear to *lapis lazuli*. The so-called white resist for cylinder printing consists, as an example, of acetate or sulphate of copper, acetate of lead thickened with gum, or dextrine solution. This composition having been printed by means of the cylinders, the pieces are the next day put into the indigo-vat and kept there until the desired depth of colour has been obtained, after which they are passed through a bath containing dilute sulphuric acid until the places where the resist has been applied have become white. The *rationale* of this process is the following:—As soon as the reduced indigo (white indigo) in the vat comes in contact with the oxide of copper, it is converted at the expense of the oxygen of the oxide into blue indigo, which is precipitated in insoluble state on the resist. By the treatment with dilute sulphuric acid the hydrated sub-oxide (red oxide) of copper is dissolved, and with it the indigo blue washed out.

Instead of the salts of copper white resists are used, and composed of bichloride o. mercury and sulphate of zinc; the former acts in a manner similar to the salts of copper, while the latter enters into an insoluble combination with the reduced (white) indigo, which is precipitated where the resist has been applied.

Discharges.

Discharges are for the purpose of producing by chemical means white patterns on certain parts of the dyed cloth. This end may be attained by dissolving a previously applied mordant or—as is the most usual method—by destroying or discharging the dye which has been distributed over the whole surface of the cloth. As regards the first method, certain acids—phosphoric, arsenic, lactic, oxalic, hydro-fluosilicic acids—are made to combine with the base contained in the mordant; while for the purpose of discharging the previously applied colour, there are used such substances as bleaching-powder, chromic acid, a mixture of red prussiate of potash and caustic soda-ley, permanganate of potash, a paste composed of bromine mixed with water and pipe-clay, nitric acid, &c. All these agents have an oxidising effect, whereas protochloride of tin and protosulphate of iron, also used for this purpose, acting by absorbing oxygen, are reducing substances. Among the acids, tartaric acid is generally used for the purpose of discharging alumina and oxide of iron employed as mordants; sometimes this acid is mixed with bisulphate of soda. A piece of cloth dyed red or blue, to which is in certain parts applied a mixture of tartaric acid, pipe-clay, and gum (the latter as thickening to give consistency), becomes immediately bleached when the cloth so prepared is immersed in a solution of bleaching-powder.

Acid Discharges.

Oxidising Agents as Discharges.

Of late fluoride of potassium has been used as a discharge for Berlin blue. The discharging of indigo blue by oxidising agents is due to the formation of isatine from the indigo blue, the former being soluble, the latter insoluble in water, so that the soluble substance can be removed by washing:—

$$\underbrace{C_{16}H_{10}N_2O_2}_{\text{Indigo blue.}}+2O = \underbrace{C_{16}H_{10}N_2O_4}_{\text{Isatine.}}.$$

Indigo is discharged by chromic acid, employed in practice as bichromate of potash, the acid being reduced while giving off oxygen to chromic oxide. More recently Mercer has proposed to bleach goods dyed with indigo by the application of a mixture of potash and ferricyanide of potassium; for this purpose the indigo-dyed cloth is soaked in a solution of red prussiate of potash, and then caustic potash thickened with British gum is printed on. The potash converts the ferricyanide into ferrocyanide, and by the oxygen thus set free the indigo blue is coverted into isatine:—

$$\left.\begin{array}{l}\text{Ferricyanide of potassium, } 4K_3FeCy_6\\ \text{Caustic potash, } 4KOH\\ \text{Indigo blue, } C_{16}H_{10}N_2O_2\end{array}\right\}\text{yield}\left\{\begin{array}{l}\text{Ferrocyanide of potassium, } 4K_4FeCy_6.\\ \text{Isatine, } C_{16}H_{10}N_2O_4 2H_2O.\end{array}\right.$$

Reducing Agents as Discharges.

Protochloride of tin, known as crystals of tin and as tinsalt, is the most important of the reducing agents applied to goods dyed with oxide of iron. When the protochloride is placed in contact with oxide of iron, the result is the formation of readily soluble protochloride, which is removed by washing, while simultaneously there is deposited on the fibres of the cloth stannic acid (more correctly proto-peroxide of tin), which may serve as a mordant for red and yellow dyes.

Calico Printing. Calicos may be printed by:—

1. Dyeing in the dye-beck.
2. By block or cylinder printing (topical colour-printing).
3. By resist or discharge printing.

In the process of dyeing in the dye-beck (madder style) the thickened mordant, to which usually some faint colouring matter is added for the purpose of recognition (the reader should bear in mind that the mordants are colourless, or at least nearly so), the pattern produced on the white calico is imprinted by the aid either of blocks or cylinders, upon which the desired pattern is engraved.

The process of block printing takes place upon a table over which a piece of thick woollen cloth is stretched. The calico to be printed is laid on this cloth, and by the aid of blocks the mordant is transferred to the calico. The blocks, made of pear-tree wood, box-wood, or fir-wood, have the pattern engraved *en relief*, or wrought by means of brass wires fastened in the wood in such a manner as to form a certain figure. The former blocks are called engraved, the latter dotted or stippled blocks, while in some cases the two methods are used simultaneously. In order to distribute the mordant uniformly a frame or chase is employed, on which, by means of nails, a stout piece of canvas is stretched, the frame being made to float on the top of a thick solution of gum or linseed mucilage, placed in a suitably constructed vessel. On a frame a piece of oil-cloth is fastened to prevent percolation of the fluid; next the mordant is brushed over the cloth of the frame quite uniformly. The printer puts his block on the cloth thoroughly moistened with mordant, so that the projecting engraved portions of the block become uniformly moistened, and the block having been transferred to the calico is pressed thereon, the pressure aided either by a smart blow given by the printer's fist or by a wooden mallet, care being taken to print every portion of the engraving equally on to the woven fabric. When several mordants are placed on to the frame by the aid of separate brushes and thence printed on to the cloth, the result is the production of the so-called *iris* or *fondu* prints. In order to accelerate the operation of printing, machinery is now usual—for instance, the Perrotine, invented by Perrot, at Rouen, in 1833. This machine works with three to four wooden formes (Perrotine formes upon which the patterns are fastened by nails), these patterns being cast in a manner similar to stereotype plates, consisting of a readily fusible metallic alloy. The arrangement of this machine is of course such, that the formes are as wide as the cloth intended to be printed. Instead of this machine cylinder printing has become general. The cylinders are made of copper, and on these the pattern is engraved. The cylinders are revolved in a framework by means of machinery. By the aid of a wooden cylinder covered with cloth which dips into the vessel containing the mordant, the copper cylinder is fed with mordant, while a kind of blunt knife, known technically as the doctor, scrapes off from the non-engraved portion of the copper cylinders any superfluous colour, which is thus confined to the engraved portion forming the design.

Before the mordanted cloth can be dyed it has to be kept for some time in order that the alumina and iron mordants may combine intimately with the fibre of the cloth. Moreover, the cloth, before being immersed in the dye-beck, has to undergo the operation technically known as cleansing; that is to say, after the mordant has become dry, the thickening and faint colouring matter have to be removed, together with any mordant uncombined with the fibre. For goods intended to be madder dyed the cow-dung bath is required. Usually some chalk is added for the purpose of saturating the acetic acid or the mordant. Although all calico printers agree that the cow-dung bath is necessary, the *rationale* of the action of this bath has not as yet been explained. According to Mercer and Blyth, for cow-dung may be substituted certain phosphates and arseniates, and these chemists propose the use of phosphate of soda and phosphate of lime. More recently silicate of soda has been used instead of cow-dung. In England cow-dung is no longer, or at least only very rarely, used. After the goods have been treated with cow-dung or its substitutes, they are washed and then dyed. In the case of dyes the colouring matter of which is readily soluble in water, infusions or decoctions are used; cochineal, quercitron bark, weld, safflower, &c., are thus used. But other dyes, the colouring principle of which is less readily soluble, such as madder and garancine, are put with hot water into the dye-beck in which the mordanted goods are immersed. It is clear that when several different mordants have been printed on to the cloth, several different colours can be obtained by the same dye material. With madder, for instance, all shades of pink and red, black, brown, violet, and lilac can be produced when alumina and iron mordants and mixtures of these have been used as mordants. As the dye only takes where the mordant has been applied, it can be readily removed from the other portions of the cloth; this removal of superfluous dye is effected by washing, treating with bran and soap, and grass bleaching operations, technically termed clearing. In some cases madder-dyed goods are cleared with the aid of solutions of bleaching-powder or Javelle ley (see p. 223). Some dyes require in order to become bright and brilliant the operation known as *avivage* or clearing, but of a special nature; this is more particularly applicable to Turkey-red dyed goods, which after removal from the dye-beck are submitted to a boiling under pressure with soap-suds and chloride of tin.

Topical or Surface Colours. The process of applying thickened colours and mordants simultaneously is known as topical or surface printing, the colours, pigments, being termed topical or surface colours. Of these two varieties are known, one of which is printed in the state of solution, becoming gradually fixed and insoluble on the fibre itself; the other is applied in the insoluble state with thickening and plastic substances, by the aid of which the colours adhere to the fibre, so that by simple washing they are not removed—ultramarine is applied in this manner. Many of these styles of printing require for fixing as well as for clearing the application of steam, from which they derive their name of steam colours, now very extensively used. The printed goods are dried for two or three days, and next stretched on frames, and thus arranged exposed to the action of steam at 100°, in properly constructed rooms. The length of time this operation is continued depends in practice upon several conditions, and varies in different establishments, but is generally twenty to forty-five minutes at a time. The precise action of the steam is not well known. China blue, deriving its name from a resemblance to the colour of old china ware, is produced by a very complex process, of which the following is a brief outline. The indigo in its natural state is very finely ground and mixed with deoxidising bodies, such as sulphate of iron, acetate of iron, orpiment, or protochloride of tin, and thus applied to the cloth; the goods thus printed are aged and afterwards dipped into clear lime-water; this serves to "wet out" and to form an insoluble, or at least difficultly soluble, compound of the gum paste or starch of the thickening with the lime. The piece is next placed in the copperas vat for ten minutes, the lime-water which adheres to the cloth precipitating a little oxide of iron over its whole surface, but it does not appear that the slightest dissolution or deoxidation takes place. The piece is now taken to the lime vat again, in which it is gently moved about; by this operation the indigo is deoxidised and dissolved, but does not spread beyond the design, for the reason that it is surrounded with fibres saturated with water and coagulated gum, while by the excess of lime present, the solubility of the deoxidised indigo is greatly lessened. The piece is again dipped into the copperas vat and again into the lime vat several times, the last dip being in lime for a long time. The goods, thickly coated with a cream of lime, are put into clean water, and afterwards into a dilute acid, then washed and cleared in weak soap and warm weak acid. China blue is a fast colour, but very dark shades cannot be obtained by this process, which is rather costly on account of the time and labour it requires. Steam blue is obtained by printing with a solution of ferrocyanide of potassium thickened with starch, acidulated with tartaric acid and a small quantity of sulphuric acid, after which the calico is dried, aged, and lastly steamed. Yellow is produced by first treating the goods with acetate of lead, and next passing them through a solution of bichromate of potash. Green is produced with a mixture of chromate of lead and Berlin blue.

Discharge Style. As employed in practice on the large scale, the term discharge is given to a composition which has the power of bleaching or discharging the dye already communicated to a fabric. The discharging of mordants by the aid of agents—chiefly acids—which dissolve or otherwise render ineffective the constituents of the mordants, seldom occurs in practice, and only then a few special styles. As a rule, discharge is effected with uniformly dyed goods, more especially indigo and Turkey-red dyed fabrics, upon which it is desired to produce white patterns; while sometimes upon a portion of the white ground thus obtained other colours are produced. The agents used to produce the discharge vary with the dye which has been applied as well as with the colour afterwards desired to be produced on the white ground, while, moreover, the discharge ought not to injure the fibre of the cloth. Oxalic, tartaric, citric, more or less dilute sulphuric and hydrochloric acids, bisulphate of potash, nitrate of lead, solutions of bleaching-powder, weak chlorine water, and bichloride of tin are used, being properly thickened with suitable materials, while some are so contrived as to serve as mordants for colours to be subsequently applied; for instance, for blue, a mixture of tartaric acid, Berlin blue, tinsalt, farina, and water, is used; for yellow, nitrate of lead with tartaric acid, starch, and water; for green, a mixture of yellow and blue; for black, a logwood decoction to which nitrate of iron has been added. The pieces thus prepared (these discharges having been printed on) having been put into and passed through a solution of chloride of lime, the dye previously applied is destroyed where the discharge is printed, and in its stead the new colour is produced according to the pattern. Chromic acid, or an acidulated solution of bicromate of potash, is sometimes used as a discharge, the oxide of chromium produced yielding a brown colour.

Aniline Printing. As regards the application of these colours to calico printing they may be termed steam colours. The printing and fixing is effected by the following methods:—1. The thickened mordant is printed on, and next fixed either by drying or by ageing and steaming after drying, the fabric being dyed in a solution of the aniline colour (red, violet, blue), the colour becoming fixed to the mordanted portions only of the calico. 2. The thickened mordant is mixed with the aniline dye, and thus printed, and the fixing effected by steaming. The mordants for these colours are:—Dried albumen, blood albumen, viz., that bleached by the action of ozone obtained by means of oil of turpentine; vegetable gluten in various forms, for instance, that dissolved according to W. Crum's plan in weak caustic soda ley, or according to Scheurer-Rott in a weak acid, or gluten dissolved in saccharate of lime according to Liès-Bodard, or finally gluten dissolved by incipient putrefaction, as suggested by Hanon. Instead of gluten caseine may be used dissolved either in caustic ley or in acetic acid; glue and tannate of glue are also used (Kuhlmann and Lightfoot). Other mordants for these colours are tannin, fat oils, and preparations thereof, as oleo-sulphuric acid, palmatino- and glycerin-sulphuric acid. Further, certain resins, among which shellac dissolved in borax is one.

Gluten is largely obtained as a by-product of the preparation of starch from wheaten or other flour. When required for use as a mordant, the gluten is allowed to remain in moist state, and by incipient putrefaction becomes sour, and hence fluid. The mass is purified by first treating it with carbonate of soda; 5 kilos. of the sour gluten require for saturation about 560 grms. of a carbonate of soda solution at 1·15 sp. gr., whereby the gluten is again rendered insoluble, and after having been washed is re-dissolved in caustic soda ley, 5 kilos. of the gluten requiring 435 grms. of a caustic soda solution at 1·080 sp. gr. This solution is next diluted with 3·5 litres of water. The fluid is printed on the calico, which is next dried, aged, and steamed, after which it is rinsed in water and dyed in a solution of the aniline colour. The gluten is sometimes mixed with the aniline colour and printed on with it, after which the calico is steamed a first time, then washed, and steamed a second time. Gluten may be used without the preparation with carbonate of soda by leaving it to putrefy until it has become very fluid; it is then mixed with about one-third of its weight of caustic soda solution of the above 1·080 sp. gr. When caseine (lactarine, it is technically termed in England) is used for mordanting calico previous to the application of aniline dyes, it is dissolved in caustic soda, and after the calico has been printed with this mixture the aniline colour is printed on.

The method of printing with aniline colours as devised by (3) Gratrix and Javal, differs considerably from the preceding, and consists (*a*) in preparing an insoluble compound of the aniline colour with tannic acid, which, having been thickened with Senegal gum, is printed on to the cloth which has been previously mordanted with tinsalt or any other suitable mordant; or (*β*) there is printed on the previously animalised cotton, that is to say, cotton mordanted with albumen, lactarine, or gluten, or cotton mordanted with tinsalt, a thickened decoction of galls, by which in the first place a tannate of albumen, &c., in the second one of tin, both insoluble in water, are formed. The calico having been dried is then passed through an acidulated aniline solution. The aniline-tannin compound mentioned under (*a*) is prepared by adding to an aniline solution as much decoction of galls (better still solution of tannin) as is required for the complete precipitation of the dye material. This precipitate is collected on a filter, washed, and dissolved in alcohol or acetic acid, and having been thickened with gum, the solution is used for printing. When printed the goods are steamed and washed either with or without soap, according to the shade which it is desired to give to the colour. A red colour requires a soap-wash. According to the second method the calico is treated with a solution of stannate of soda, after which a thickened solution of tannin, or a tannin-containing material is printed on to the cloth, which is steamed and the mordant further fixed. The dyeing operation is carried on in a dye-beck used as for madder, the beck being filled with water, acidulated with acetic acid, and heated to 50°. The cloth is put into this liquid, and gradually the dye dissolved in acetic acid is added. When the requisite quantity of the dye has been added, the contents of the dye-beck are heated to the boiling-point. Aniline black is produced (see p. 579) upon the cloth by means of chlorate of potash, chloride of copper, ferricyanide of ammonium, or freshly precipitated sulphuret of copper. Naphthylamin violet (see p. 583) is now produced by a similar process.

Hotpressing, Finishing, and Dressing. The printed, washed, and rough-dried cotton goods are next finished, that is to say, starched, dried, often calendered, hot-pressed, folded, and again pressed. In England these operations form a distinct branch of the dyeing art usually not performed by the printers. For chintz white wax is added to the hot starch in order to impart a better gloss. In order to give muslins a somewhat velvety appearance spermaceti is added to the starch while being boiled with water.

Printing Linen Goods. Linen goods are, as a rule, neither dyed nor printed, and only a few indigo-dyed articles on which white patterns are produced are in the trade.

Printing Woollen Goods. As regards the printing of woollen goods, flannels more particularly, block-printing is most frequent. The goods are mordanted with chloride of tin. The fixing of many of the colours imparted to woollen goods is effected by steaming. We distinguish, moreover, in the printing of woollen goods—1. Golgas printing; and (2) Berill printing. As regards the former method, now almost obsolete, the golgas, a very thin and light flannel fabric, is first mordanted with alum and cream of tartar, and next placed between wooden or leaden plates partly perforated with a pattern, and strongly pressed in a peculiarly constructed hydraulic press, where it is possible to force dye solutions through the goods, which are only wetted by these solutions and consequently dyed where the dye liquor can pass through, the strong pressure preventing the liquid running over the flannel in any other direction. By the berill printing process the surface colours, thickened with starch, are printed on to the flannel with hot brass formes; the starch not being removed, the result is the formation of relieved and coloured patterns.

Printing Silk Goods. The processes and methods of printing silk goods are generally the same as for calicos; either surface printing is resorted to with fixing by steam, or various mordants are printed on to the silk, which is next dyed in the dye-beck. A peculiar kind of printing on silk is based upon the property of nitric acid producing upon silk a permanent yellow colour, as well as of destroying most other dyes, and yet acting on resins and fatty substances only slowly.

Mandarin Printing. This mode of printing on silk is termed mandarin printing, and the tissue, chiefly silk handkerchiefs, to which it is applied, mandarins. In order to etch with nitric acid on the indigo-dyed silk, there is printed on to it a resist, composed of resin and fat, after which the tissue is kept for 2 to 3 minutes in a mixture of 1 part of water and 2 parts of nitric acid heated to 50°. The goods are then thoroughly rinsed in fresh water and boiled in a soap solution, to which carbonate of potash is added. The portions of the silk where no resist has been placed are thus made beautifully yellow.

Bandanas. On genuine madder-red dyed silk white patterns are etched by a process similar to that just described for golgas printing. The goods are placed between leaden plates in which the pattern is cut out, and then submitted to strong hydraulic pressure; next a solution of bleaching-powder acidulated with some sulphuric acid is forced through the goods, by which the madder dye is destroyed. The pattern thus etched may be after washing, the pressure remaining and water being forced through, dyed yellow by first forcing a solution of acetate of lead and next one of chromate of potash through the woven fabrics, kept of course in the press.

DIVISION VII.

THE MATERIALS AND APPARATUS FOR PRODUCING ARTIFICIAL LIGHT.

Artificial Illumination in General. Very few among the large number of bodies which at a high temperature, either by combustion or at a red heat, evolve a permanent light are suited for use as materials for artificial illumination. The number of bodies which comply with the conditions demanded in artificial illumination is very small. These conditions are the following:—

1. That by the combustion of the body a sufficient degree of heat be evolved to maintain the combustion. 2. That when the burning body happens to be solid, it be previous to the combustion converted into gas or vapour, as otherwise no flame is generated, which is absolutely required for the purpose of illumination. 3. That the burning body evolve in the flame solid bodies or very dense vapours as an essential condition of the illuminating property of the flame. 4. That either the body itself or the raw material from which it is obtainable be present in large quantity and be readily obtainable. 5. That the products of combustion be gaseous and harmless to the health.

It is a generally known fact that any great accumulation of heat imparts to bodies the property of emitting light. This is more conspicuous in solid and fluid bodies, because their molecules are placed more closely together than happens to be the case with gases and vapours. At a temperature of 500° to 600° a solid body becomes red-hot, while at about 1000° white heat occurs. A gaseous body heated to these degrees of temperature emits only a very feeble light. In order to render a gaseous body (and as already mentioned only gaseous bodies are suited for illuminating purposes) luminous during its combustion, it should contain the vapours of some of the higher hydrocarbons (for instance, benzol, acetylen, naphthaline, &c.), and that these by becoming white-hot should yield light, or that there be present in the flame, by itself non-luminous, a solid body which is thus rendered white-hot; for instance, a spiral platinum wire in a hydrogen flame, a piece of caustic lime in the oxy-hydrogen flame, a cylindrical piece of zircona or magnesia in a hydrogen or coal-gas flame fed by oxygen, oxide of magnesium in the flame of burning magnesium (magnesium light), solid phosphoric acid in the flame of burning phosphorus, &c. Leaving out of the question for the present such lights as are not generally available, as those just alluded to, and also the electric light, it is clear that for all practical purposes we can avail ourselves of only such materials for illuminating purposes as yield a flame which emits light in consequence of the vapours of heavy hydrocarbons present therein. These hydrocarbons are indeed contained in all the substances which are either used for illuminating purposes or from which illuminating materials are prepared, as, for instance, tallow, palm oil, and the fatty acids, viz., stearic and palmitic, wax, spermaceti, paraffin, rape-seed oil, the various paraffin and petroleum oils, camphine (highly rectified oil of turpentine), coals. bituminous schists, boghead coal, wood, fats, and resins.

Flame. Every solid and fluid body which becomes either volatilised, or decomposed into gaseous matter at a temperature below that required for its combustion, can burn only in the shape of gas. The ensuing light is what we call flame.

The well-known shape of flame is due to the pressure of the ambient air, because the latter, becoming heated and being rendered specifically lighter, ascends. When the illuminating material consists of molten paraffin, stearic acid, or oil (colza, rape-seed, or petroleum), it is sucked upwards in the interstices of the wicks acting as capillary tubes, and in the immediate neighbourhood of the flame these substances are converted into gases and vapours, the nature of which closely agrees to that of purified illuminating gas.

Sir Humphry Davy was the first to elucidate the nature of flame and the cause of its luminosity as well as of the unequal luminosity of different kinds of flames. In our day the researches of Hilgard, H. Landolt, Pitschke, Blochmann, Kersten, and more particularly of H. Deville, Volger, Lunge, Dr. Frankland, and others, have greatly contributed to our knowledge of flame. When closely observed we can distinguish in flame three distinct portions, viz.:—(1) an outer luminous layer, or so-called veil; (2) a central nucleus, which is red-hot; and (3) an inner and lower portion, in which the gaseous substances about to become ignited are heated. The opinion formerly held about the cause of the emission of light by flame was that by the combined action of a very high temperature and the oxygen of the atmosphere, which first combines with the hydrogen, carbonaceous matter is separated, which, being heated to a bright white heat emits light. By the researches made by Hilgard on the flame of burning candles, and of Landolt and H. Deville, who experimented with a gas-flame, we have been taught that a very quick and rapid diffusion of air and the products of combustion takes place, and that in the interior of the flame a decrease of the quantity of the combustible gases and an increase of the products of combustion occurs. But all these researches do not enable us to explain many of the most ordinary phenomena observed in luminous flames. We do not, for example, know what relation there exists between the chemical composition of an illuminating substance and its illuminating power; consequently, gas analyses made for the purpose of testing gas are in that respect of very little value. According to the researches of O. Kersten, confirming those of O. L. Erdmann, the atmospheric oxygen combines, at least in gas flames, first with the suspended particles of free carbon and next with the hydrogen. The combustion, Kersten states, does not take place in the centre of the flame, but only at the veil and that portion of the luminous mantle which is nearest to the veil, because we cannot admit that any trace of oxygen can pass through a layer of red-hot hydrogen and carbon. The products of combustion observed in the centre of the flame are not formed there, but have been carried there by diffusion. The total heat of the flame is consequently derived from the limit of the zone of combustion. The temperature of the centre of the flame and of the mantle increases of course towards the top, and hence the most luminous portion of the flame is that where the carbon is separated by the intense heat, below the thin layer of the dark central cone. Higher, where the heat which decomposes the hydrocarbons into their constituents reaches upwards to the middle, the entire centre is luminous, and hence a solid flame is exhibited. As, then, the free carbon comes nearer to the layer rich in oxygen, it is converted into carbonic acid, and is the more luminous the more energetic this combustion. In the veil oxide of carbon and hydrogen burn simultaneously. The reason why this veil does not exhibit at its lower part a luminous mantle is because the mass of the gases in the interior is too cold for admitting a separation of hydrocarbons.

The non-luminosity of a flame, even that of pure olefiant gas, due to the too contracted space occupied by the temperature of the veil, may be observed when a gas flame is turned down as low as possible; in this case a complete combustion takes place before any decomposition can ensue, just as happens in the lower blue portion of a luminous flame. The luminosity, therefore, depends upon the composition of the gas before it is burnt, and not upon a subsequent combustion of the carbon. It has been assumed that the luminosity of gas flames is due to the momentarily eliminated particles of solid carbon becoming white-hot; but according to Dr. Frankland's researches, made in 1867, it is not the particles of solid carbon, but rather the dense vapours of the higher hydrocarbons, those having a high boiling-point, which, while ignited at an elevated temperature, cause the luminosity of the gas flame. There are present in illuminating gas compounds of great density, which in the state of vapour, similar to what may be observed of the vapour of arsenic, may render flame luminous; among these are the vapours of benzol, naphthaline, and probably of many other of the constituents of coal-tar. These vapours remain in the flame in undecomposed state up to the moment that they reach the outer layer or envelope of the flame, where they become consumed when coming in contact with the oxygen of the air. It has been customary to adduce as a proof that the luminosity of the flame is due to eliminated particles of carbon, the fact that when a piece of porcelain is held in the flame carbon is deposited thereon; but it has not been proved that this substance is pure carbon; on the contrary, when the deposit is submitted to analysis, it is always found to contain hydrogen, and any chemist who desires to obtain pure carbon from lamp-black knows well enough that this substance has to be strongly ignited in close vessels before all the hydrogen it contains has been eliminated. In order to accelerate this process of purification, chlorine gas is passed over the lamp-black placed in a combustion-tube, or better, a porcelain tube, and raised to nearly a white heat. Lamp-black is probably nothing more than a conglomerate of the densest light-emitting hydrocarbons, the vapours of which become condensed upon the surface of the cold porcelain. · How could a flame be so transparent as it really is were it filled with solid particles of carbon? How could it be the same for photometrical assays if the flame be placed with its broad or narrow edge towards the photometer if the light of the flame were due to solid particles of carbon? It is possible that in a slight degree an elimination of carbon actually takes place as a consequence of the decomposition of hydrocarbons, but the main source and cause of the luminosity of a gas-flame is the combustion of the heavy hydrocarbons. It is clear that the temperature of the flame has some influence on its luminosity. According to H. Deville's experiments (1869) the degree of the luminosity of a flame is intimately connected with the density of the vapours present therein, while the dissociation does not appear to be without some influence upon the condition of the flame. Under ordinary conditions an illuminating material to be burnt in air free from draughts, and so that no smoky flame be produced, should contain upon 6 parts by weight of carbon 1 part by weight of hydrogen, as nearly obtains in olefiant gas, paraffin, wax, and stearic acid. Oil of turpentine, which contains upon 1 part by weight of hydrogen 7·5 parts by weight of carbon, burns with a sooty flame. This is the case in a higher degree with benzol, which upon 1 part of hydrogen contains 12 of carbon, or with naphthaline, in which the proportion is 1 : 15. In order to burn the excess of carbon (as already stated, according to Dr. Frankland's researches, this is not pure carbon, but a conglomeration of dense hydrocarbons) which becomes eliminated, an increased supply of air is required, such as is created by a lamp-glass. Such flames as do not eliminate carbon, as, for instance, those of marsh-gas and alcohol, yield only a faint light when burning. The luminosity of gas is at once destroyed when atmospheric air is mixed with the gas, as may be observed in the Bunsen burner; the same effect obtains when the gas is mixed with other indifferent gases or vapours.

Artificial light is procured:—

I. From substances solid at ordinary temperatures, and prepared in the shape of candles made of such materials as tallow, palm oil, stearic, palmitic and elaidic acids, wax, spermaceti, and paraffin.

II. By employing fluid substances, chiefly in lamps, and which may be brought to the following categories:—

- *a*. Non-volatile oils, such as rape-seed, olive oil, fish-oil.
- *b*. Volatile oils which are either—
  - *α*. Essential oils, as, for instance, camphine (refined oil of turpentine); or
  - *β*. Mineral oils, obtained from tar, from peat, lignite, bituminous slate, boghead coal, and consisting of mixtures of fluid hydrocarbons, met with in commerce under a variety of names, such as solar oil, photogen, ligroine, kerosen, paraffin oil, &c.; or
  - *γ*. Native earth-oil or petroleum, which, after having been refined, is sold in England, commonly under the name of petroleum oil, to distinguish it especially from Young's patent paraffin oil.

III. By means of gaseous substances obtained by the dry distillation of coals, bituminous slate, peat, wood, petroleum residues, resins, and fatty substances, all of which when submitted to a high temperature above a cherry-red heat, become decomposed, yielding a solid residue rich in carbon (coke), tar, and gases; or again, by other modes of treatment, as with the so-called water-gas, obtained by passing steam over red-hot charcoal.

In the gaseous illuminating substances the luminous body is either:—

- *a*. Yielded by the flame itself, as is the case in the ordinary gas flame; or,
- *b*. Introduced externally, as in the so-called platinum light, by the aid of platinum wire; in the lime-light by means of lime; in the magnesium- and zirconium-light from cylindrical pieces of these substances; or by the so-called carburation of the gas with the vapours of fluid hydrocarbons.

I. *Artificial Light obtained by Means of Candles.*

Light from Candles. Leaving out of the question the use in some very poor districts of splints of resinous wood for the purpose of procuring artificial light, candles are the only shape in which solid materials are employed for illuminating purposes. A candle consists of the solid illuminating material, palmitic and stearic acids, paraffin, tallow, or wax, cast in the well-known cylindrical shape, and provided in the direction of its longitudinal axis with a cotton-wick, the thickness and plaiting of which should be arranged in proper relation to the diameter of the candle. We describe in the following pages the manufacture of:—

1. Stearine candles.
2. Paraffin candles.
3. Tallow candles.
4. Wax candles.

Manufacture of Stearine Candles.

1. Palm-oil and tallow are now in Europe the raw materials for the manufacture of these candles, while lard is used for this purpose in the United States (Cincinnati). The researches of W. Heintz, which complete those made by Chevreul, have taught us that these fats consist of palmitic, stearic, and oleic acids, and glycerine. The acid which Chevreul has designated as margaric acid has been proved to be a mixture of palmitic and stearic acids. The so-called "stearine candles" are frequently made of a mixture of stearine (viz., a mixture of palmitic and stearic acids) and soft paraffin. Candles of this description are known abroad as Apollo and Melanyl candles. The manufacture of stearine candles consists in two chief operations, viz.:—

A. The preparation of the fatty acids;
B. The conversion of these acids into candles.

A. The preparation of the fatty acids can be effected by saponification with lime, by means of sulphuric acid and subsequent distillation, by means of water and high-pressure steam, and by means of steam and subsequent distillation.

Preparation of Fatty Acids by Means of Lime.

I. *Saponification of the Fats by Means of Lime.*—The raw fats employed in this operation are beef or mutton tallow, and palm oil. The mutton tallow contains a larger quantity of solid fatty acids, and is more readily saponified, but beef tallow is cheaper. The Russian tallow, of which large quantities are met with in commerce, is usually a mixture of beef and mutton tallow. As palm oil is imported into Europe in large quantities and is comparatively low in price, it has become in many stearine candle manufactories the fat chiefly used.

Stearine yields	95·7	parts of	stearic acid	(melting at	70°)	$C_{18}H_{36}O_2$.
Palmitine ,,	94·8	,,	palmitic acid	,,	62°	$C_{16}H_{32}O_2$.
Oleine ,,	90·3	,,	oleic acid	,,	−12°	$C_{18}H_{34}O_2$.

Stearine, palmitine, and oleine, are glycerides. The stearine is tri-stearine, $C_{57}H_{110}O_6$; palmitine is tri-palmitine, $C_{51}H_{98}O_6$; and oleine is tri-oleine, $C_{57}H_{104}O_6$. By the saponification with milk of lime, the calcium salts of the three fatty acids, stearic, palmitic, and oleic, are formed, and glycerine is separated. The operation of saponification is conducted in the following manner:—Of tallow or of palm oil about 500 kilos. with 800 litres of water are put into wooden lead-lined vats or tuns, of 20 hectolitres cubic capacity, and next by the aid of steam conveyed into the vessel by a leaden pipe coiled spirally. When all the tallow has been melted there are gradually added to it some 600 litres of milk of lime, containing 70 kilos. of lime = 14 per cent of the weight of the tallow, care being taken to stir the mixture continuously. After heating for some six to eight hours the formation of the lime-soap is complete. The somewhat yellow glycerine solution is run off from the solid granular lime-soap and used for preparing glycerine. According to theory, starting from the supposition that upon 3 molecules of fatty acids found combined in the neutral fat there is 1 molecule of glycerine, 100 parts of fat would require only 8·7 parts of caustic lime, but in practice 14 per cent of lime is generally used because it has been found that the saponification is rendered easier, but a larger quantity of sulphuric acid is also required.

The lime-soap thus obtained is decomposed by means of sulphuric acid, either concentrated, or as so-called brown or chamber acid. This operation is carried on either in the vessel in which the saponification took place, or in a similarly constructed vessel or in stoneware basins, also fitted with a steam-pipe. The quantity of sulphuric acid required for the decomposition of a mixture composed of 500 kilos. of tallow and 70 kilos. of lime amounts to 137 kilos. The acid is first diluted with water to 12° B. = sp. gr. 1·086 (in this condition the acid contains 30 per cent, H_2SO_4), and is next poured on to the lime-soap, with which it is thoroughly stirred, while steam heat is applied simultaneously. When the fatty acids have been set free the supply of steam is shut off, and the fluid mixture left for some time, the melted fatty acids rising to the surface, while the gypsum settles at the bottom of the liquid. The melted fatty acids are transferred to a lead-lined tank, and in order to remove the last traces of lime and sulphate of lime, first washed with dilute sulphuric acid, and next with water, the steam heat being kept up to maintain the acids in a fluid state. The quantity of purified fatty acids thus obtained is the following:—

500 kilos. of tallow	459·5 kilos. of fatty acids.
500 " "	463·0 " " "
500 " "	478·0 " " "
500 " "	487·5 " " "
2000 kilos. of tallow	1888·0 kilos. of fatty acids,

equal to 94·8 per cent. The yield depends on the kind of tallow used, on its purity, and the mode of operating for its saponification.

100 parts of the fatty acids give:—

a. 43·3 parts of solid fatty acids	On an average 45·9 parts of a mixture of stearic and palmitic acid.
b. 45·8 " " " "	
c. 46·2 " " " "	
d. 48·4 " " " "	

When the fatty acids have been as much as possible freed from lime, gypsum, and sulphuric acid, by means of repeated washing with water, they are kept in molten condition for some time in order that the water may be thoroughly eliminated. Next, the fatty acids are cooled and become solidified, after which they are submitted to strong hydraulic pressure in order to remove the oleic acid, this operation being repeated and then performed with the aid of heat. The acids are then cast into large square blocks, or cooled in moulds similar in shape to those used for large cakes of chocolate, and capable of containing 2 kilos. of the fatty acids. In some works moulds made of enamelled iron are used for this purpose. The fatty acids are left in these moulds for the purpose of crystallising slowly; in winter twelve hours, in summer twenty-four hours, are required for attaining this end. The more slowly the crystallisation proceeds the better, because the more readily the fluid portion can be separated by pressure from the solid mass. The solidified mass is next submitted to hydraulic pressure, in order to eliminate the fluid fatty acids retained between the crystals of the solid mass. The first operation of pressing is performed at the ordinary temperature. The solid cake of the fatty acids is for this purpose put into a press-bag, which may be made of any strongly woven fabric, horsehair cloth being often employed. The press-bag having been filled is placed between plates of iron or zinc, and then transferred to the table of a hydraulic press, capable of exerting a pressure of 200,000 kilos. The oleic acid which runs off is collected in channels and thence conveyed by a pipe to a cistern. This material is used in soap-making, also for lubricating wool, and more recently as oleic acid ether mixed with alumina for the purpose of softening leather. When the hydraulic press does not remove any more fluid from the solidified crystalline acids, hot-pressure is resorted to. For this purpose hydraulic presses of a peculiar construction and placed in a horizontal position are employed; the arrangement of these presses, the plates of which are heated by means of steam is, however, too complicated to be usefully described. The pressed fatty acids are next purified. This is effected by treating them in a molten state with very dilute sulphuric acid (3° B. = 1·020 sp. gr.), and washing them with water, an operation repeated two to three times, the fatty acids being of course kept molten all the time. The wash-water to be employed for this purpose ought to be free from lime, and if such water is not obtainable, the lime should be removed by means of oxalic acid. The purified fatty acids are next maintained in a molten state for some time, in order to eliminate the water mechanically adhering to them. Sometimes the fatty acids are clarified by the aid of white of eggs beaten to a froth, and added to the water of the last operation, in the proportion of 2 eggs to 100 kilos. of fatty acids; or the stearic acid is re-molten in water containing oxalic acid. The fatty acids thus obtained are either cast into thick slabs and thus sent to the candle factory, or the molten acids are directly converted into candles.

It is evident that annually a large quantity of worthless gypsum must result as a by-product of the decomposition of the lime-soap by the use of sulphuric acid. It may therefore be worth while to suggest that caustic baryta should be substituted for lime, because by the decomposition of the baryta-soap with sulphuric acid, there would be formed baryta white (sulphate of baryta), the value of which will cover the expense of the sulphuric acid; but, on the other hand, caustic baryta is a great deal more expensive than caustic lime. It is true that the sulphate of baryta separates more readily and completely from the liquor, and a purer glycerine can be obtained from it. Cambacère's suggestion (1855) to saponify with alumina was made with the view of obtaining a more valuable by-product. Alumina does not saponify fats, but aluminate of soda (employed for the purposes of saponification for some years in the United States under the name of natrona refined saponifier) does so, the result being the formation of an alumina-soap, while the soda is set free and may be used again for the purpose of re-dissolving fresh portions of alumina. As in the operations made with the native minerals cryolite and bauxite, aluminate of soda is obtained as an intermediate product, which may be further treated for sulphate of alumina and soda; the proposal to use an alumina-soap instead of a lime-soap deserves every consideration, the more so as the fluid obtained by the decomposition of the alumina-soap with sulphuric acid may be directly employed for the preparation either of sulphate of alumina or of alum. The alumina-soap may be decomposed at the ordinary temperature by acetic acid, and acetate of alumina obtained (see p. 263). The lime saponification process has been in a great measure thrown into the background since the invention of the far more profitable saponification process with sulphuric acid and superheated steam.

Saponification with Less Lime.

II. *Saponification Process with a Smaller Quantity of Lime and the Application of Superheated Steam.*—De Milly has essentially changed the process of the saponification of the neutral fats; he found that the quantity of lime used in the saponification, which in his works at Paris had been already diminished from 14 to 8 or 9 per cent of the quantity of the fats, could be decreased even to 4 or to 2 per cent, provided the mixture of lime-water and fatty matter was heated to a higher temperature than that usually employed. De Milly put into a steam boiler 2300 kilos. of tallow and 20 hectolitres of milk of lime, which contained either 50 kilos. of lime = 2 per cent, or 69 kilos. = 3 per cent, after which this mixture was heated to 172° by means of steam, having a temperature of 182° = 10 atmospheres, or 150 lbs. pressure per square inch. The result was, that after seven hours the saponification was complete, the contents of the boiler consisting partly of an aqueous solution of glycerine, partly of a mixture of free fatty acids, and a small quantity of a lime-soap. The boiler having been emptied was again filled, and the operation repeated so that in twenty-four hours 6900 kilos. of tallow could be operated upon. It is evident that this method of saponification is very profitable, in consequence of requiring much less sulphuric acid for decomposing the lime-soap.

Several opinions have been enunciated explanatory of this process; but if we bear in mind (1) that kind of action which Berzelius designated as catalytic, where a comparatively very small quantity of any substance may call forth a decomposition under favourable conditions of a very large quantity of another substance; and (2) recollect that Wright and Fouché have more recently (De Milly's experiments were made about twenty-five years ago) found that water at a high temperature causes the dissociation of fats and oils into glycerine and fatty acids, it is clear that while the small quantity of lime may have facilitated the saponification, the result obtained by De Milly is mainly due to the very high temperature of the water employed in the operation. This is clearer from the fact that a process of saponification is successfully in use based solely upon the application of water at a high temperature.

Saponification by Means of Sulphuric Acid.

III. *Saponification by Means of Sulphuric Acid and Subsequent Distillation by Means of Steam.*—It was known to Achard, in the year 1777, that the neutral fats are decomposed by concentrated sulphuric acid in a manner similar to the decomposition effected by caustic alkalies. This fact was again brought forward in 1821 by Caventon, and 1824 by Chevreul, but was not scientifically investigated until 1836 by Frémy, and not industrially applied until the year 1841, when Dubrunfaut introduced the distillation of the fatty acids on the large scale. The crude fatty matter usually submitted to this process of saponification is of the kind that cannot be saponified by the lime process by reason of its impurities; thus, for instance, palm and cocoa-nut oil, bone and marrow fat, fat of slaughter-houses, kitchen-stuff, the products of the decomposition, by means of sulphuric acid, of the soap-water obtained from wool-spinning and cloth-making works, residues of the refining of fish and other oils, residues of tallow-melting, &c.

This process of saponification by means of sulphuric acid as carried on in the large establishment for stearine candle-making of Leroy and Durand, at Gentilly, near Paris, consists of three operations, viz.:—

α. Saponification with sulphuric acid.
β. Decomposition of the products of saponification.
γ. Distillation of the fatty acids.

α. In order to eliminate the greatest impurities first, the crude fatty matters are molten and kept in the liquid state for some time, so that the coarser impurities may subside. The fatty matters are then transferred to a kind of boiler made of iron boiler-plates lined inside with lead, and fitted with a stirring apparatus and a steam-jacket, connected by means of pipes with a steam-boiler, so that the apparatus may be heated. Into this vessel sulphuric acid at 66° B. = 1·8 sp. gr., is poured, the quantity of this fluid being regulated according to the nature of the fatty matters operated upon. Kitchen-stuff, fat from slaughter-houses, and the like require 12 per cent of their weight of acid; palm oil requires from 6 to 9 per cent according to quality. The fatty substances having been put into the vessel, the stirring apparatus is set in motion, and the steam turned on for the purpose of supplying heat to the vessel. The temperature to which the vessel is heated varies, in Price's Works, Battersea, being 177°, while at Gentilly, the heat is seldom higher than from 110° to 115°. During the operation the mass foams, becomes brown, and evolves sulphurous acid, partly due to the action of a portion of the concentrated sulphuric acid upon the glycerine, partly to its action upon the impurities present among the fatty matters. The neutral fat is converted into a mixture of sulpho-fatty acids and sulpho-glyceric acid. The saponification is complete after some fifteen to twenty hours' application of heat. According to De Milly's new process (1867) the tallow is heated to 120°, along with 6 per cent of sulphuric acid, and the action of the latter is limited to two to three minutes; it is thereby possible to obtain 80 per cent of the solid fatty acids in a condition at once fit for making candles without re-distillation, only 20 per cent having to be distilled.

β. Decomposition of the products of the sulphuric acid saponification. The mass is left to cool for three to four hours and is next transferred to large wooden tanks lined with lead, and previously filled one-third with water. At the bottom of these tanks steam pipes are fitted, by means of which the fluid contents of the vessel are soon heated to 100°. The sulphuric acid and the fatty acids are dissociated, and these bodies, partly combined with a larger quantity of hydrogen and oxygen than was present in the fatty acids from which they were formed, partly also in an unaltered condition, are found floating on the surface. After having been repeatedly triturated with boiling water, the fatty acids are tapped or poured over into a vessel filled with water heated to 40° to 50°, for the purpose of allowing the impurities to become deposited. The clarified fatty acids are next heated in a vessel placed on an open fire in order to evaporate all the water, after which they are submitted to distillation.

γ. The distillation requires several precautions. Distillation with an open fire would convert the fatty acids into oil, gas-tar, and a carbonaceous residue, if the heat were sufficiently high. But when the temperature is properly regulated, the fatty acids are protected from the direct action of the fire. Air should be completely excluded from the distilling apparatus. With these precautions the fatty acids distil over without undergoing any essential alteration. These conditions are complied with by the use of superheated steam at a temperature of 250° to 350°. The fatty acids are put into a roomy retort supported by brickwork, and fitted with a steam tube as well as a condensing tube connected with a receiver, in which the fatty acids are collected.

When the several fatty acids are fractionally collected from the beginning to the end of the distillation their melting-points are:—

From Palm Oil.		From Kitchen-stuff and Bone Fat.
1st product	54·5°	44·0°
2nd ,,	52·0°	41·0°
3rd ,,	48·0°	41·0°
4th ,,	46·0°	42·5°
5th ,,	44·0°	44·0°
6th ,,	41·0°	45·0°
7th ,,	39·5°	41·0°

The water condensed with the fatty acids runs off from the receiver through a tap. At the beginning of the operation the water constitutes half of the produce; towards the end only about one-third. With a retort capable of containing 1000 to 1100 kilos. of material the distillation takes some twelve hours. The end of the operation is indicated by the coming over of coloured products. There remains in the retort a black tarry matter, the quantity of which amounts in the case of palm oil distillation to 2 to 5 per cent, and for kitchen-stuff to 5 to 7 per cent. This residue is not removed after each distillation but left in the retort until it has accumulated to such an extent as to render its removal necessary. The first products of the distillation of palm oil saponified by means of fatty acids are so solid, that by pressure they do not yield any fluid acid, and are at once fit for the manufacture of candles. The products which come over afterwards are further purified by hydraulic pressure, re-melting, and washing with water. The substance obtained by pressure, more or less pure oleic acid, is used for soap-making only in this country, although abroad it is burnt in some kinds of lamps. The oleic acid obtained by this process is essentially different from that obtained by the lime saponification process. The quantities of fatty acids obtained by this process of saponification are the following:—

From Suint	47 to 55 per cent.
,, Olive oil residues	47 to 50 ,,
,, Palm oil	75 to 80 ,,
,, Fat from slaughter-houses	60 to 66 ,,
,, Oleic acid	25 to 30 ,,

Chloride of zinc, which in many respects (see p. 81) is similar in its action to sulphuric acid, has been proposed as a substitute for the latter. For countries into which sulphuric acid has to be imported chloride of zinc might be of greater advantage, being capable of recovery and less dangerous and difficult in transport. When, according to the researches of L. Kraft and Tessié du Motay, a neutral fat is heated with anhydrous chloride of zinc, a complete incorporation of these substances takes place between 150°

and 200°; and by continuing the heating for some time, and washing the materials with warm water, or better with water acidulated with hydrochloric acid, there is obtained a fatty matter, which on being submitted to distillation, yields the corresponding fatty acid, while only a small quantity of acroleine is formed. The chloride of zinc, becoming soluble in the water used for washing, may be recovered by evaporating the fluid. The yield of fatty acids by this process is the same as that obtained by the use of sulphuric acid, while the fatty acids also agree as to their physical properties. The quantity of chloride of zinc required amounts to 8 to 12 per cent of the fat.

Saponification with Water and High Pressure.

IV. Some sixteen years ago another agent, capable of bringing about, in a manner similar to alkalies and acids, the dissociation of fatty matters into glycerine and fatty acids, was introduced, this agent being simply superheated steam at high pressure:—

$$\underbrace{\left.\begin{matrix}C_3H_5\\3(C_{16}H_{31}O)\end{matrix}\right\}O_3}_{\text{Tripalmitine.}}+\underbrace{3H_2O}_{\text{Water.}}=\underbrace{\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3}_{\text{Glycerine.}}+\underbrace{3\left\{\begin{matrix}H\\C_{16}H_{31}O\end{matrix}\right\}O}_{\text{Palmitic acid.}}$$

The idea of submitting fatty matters to a similar method of treatment is not a new one, for in the researches of Appert (1823) and Manicler (1826) some hints are given on the decomposition of fats by means of superheated water; but the aim of these technologists was different, for in their experiments they employed steam to separate the tallow from the cellular tissue it is contained in, and for that purpose a temperature of 115° to 121° was quite sufficient, while at a temperature of 180° and a pressure of 10 to 15 atmospheres (= 150 lbs. to 225 lbs. pressure to the square inch) water can exert a far more energetic action upon the neutral fats, dissociating them and thus setting free their constituents. The knowledge of this interesting fact is due to the researches of Tilghmann and Berthelot, who almost simultaneously made this discovery in the year 1854, while shortly after Melsens, at Brussels, obtained the same result. As regards the industrial application of this discovery, Tilghmann and Melsens made further researches; their modes of operating are very similar.

Tilghmann adds to the neutral fat about to be decomposed one-third to one-half of its bulk of water, and pours this mixture into a sufficiently strong vessel in which the fluids can be submitted to the action of heat, viz., a degree nearly as high as the melting-point of lead, 320°. This vessel is so arranged that during the operation it can be closed so as to prevent on the one hand the evaporation of water, and on the other admit of a sufficiently strong pressure. The process is carried on continuously by causing the fluids to circulate through a tube heated to the required temperature. Melsens uses a Papin's digester, in which the fat to be decomposed is heated to 180° to 200°, with 10 to 20 per cent water, to which 1 to 10 per cent of sulphuric acid has been added. Wright's and Fouché's apparatus consists of two hermetically closed copper vessels placed one above the other and connected together by means of two tubes, one of which reaches nearly to the bottom of the lower vessel, and ends in the upper one just above the bottom.

The second tube is fixed into the lid of the lower vessel and passes through the upper vessel reaching nearly to its cover. The upper vessel is the steam-generator, while the decomposition goes on in the lower vessel. When it is intended to work with this apparatus, the steam-generator is filled with water nearly to the point at which the first tube ends in it. The second vessel is then filled with molten fat so that this material reaches the top of the second tube. There remains thus a free space between the fat and the lid of the second vessel, which space is termed by the patentees *chambre d'expansion*, expansion room. Heat being applied to the generator, the steam formed is carried by the second tube into the expansion room, and becoming condensed forces it way downwards through the specifically lighter fat and flows through the first tube again into the generator. In this manner the neutral fat is intimately mixed at a high temperature and under high pressure with water, and completely dissociated in a short time into fatty acid and glycerine.

Manufacture of Fatty Acids by means of Superheated Steam and Subsequent Distillation.

V. Allied to the process just described is the operation carried on by the well-known Price's Candle Company, Limited, at Battersea. Gay-Lussac and Dubrunfaut have already tried to apply to industrial purposes the fact that neutral fats are dissociated by distillation, yielding fatty acids; but notwithstanding that these *savants* employed steam, the results obtained did not answer the expectation, because a portion of the fatty matter was decomposed, yielding acroleine and leaving a carbonaceous residue. Wilson and Gwynne were more successful with their experiments, and by using a distilling apparatus similar to that described on p. 625, they obtained by means of superheated steam the complete dissociation of the neutral fats into fatty acids and glycerine; while by closely watching and regulating the temperature, they not only could completely saponify the neutral fats, but also distil the fatty acids and glycerine over without undergoing any decomposition.

The retorts have a cubic capacity of 60 hectolitres, and are heated by direct fire to a temperature of 290° to 315°. A malleable iron steam-pipe conveys steam at a temperature of 315° into the molten fatty matter. The admission of steam is continued for twenty-four to thirty-six hours according to the kind of fat. The saponification proceeds regularly and the products distil over and are collected at the lower aperture of the cooling apparatus. The fatty acids are at once fit for candle making purposes, while the glycerine is purified by a subsequent distillation with steam. As already mentioned, the proper temperature has to be scrupulously maintained, for if the temperature falls below 310°, the saponification proceeds very slowly; but if the temperature rises much above that degree, a portion of the fatty substance is decomposed and acroleine is formed in large quantity.

Candle Making.

B. The wick is a very important portion of stearine candles, and, indeed, of all kinds of candles, because in the interstices of the wick the molten fatty matter of the candle is drawn upwards to the flame. The wick ought therefore to consist of porous substances, and in the case of candles—for lamps it is not so requisite—it should be combustible.

It is essential that the wick be of uniform thickness through its entire length and free from knots or loose threads. The yarn ordinarily used for making wicks is the lightly-twisted cotton thread known in the trade as No. 16 to 20 for tallow candles, and No. 30 to 40 for stearine candles. It is evident that the more uniform the wicks the better fitted they are for capillary action, and hence, provided the illuminating material be pure enough, a uniform combustion. Formerly the wicks were always twisted, and for tallow and wax candles this is still frequently the case, the single threads being placed next to each other and then turned so as to form a very elongated spiral. In order to obviate the snuffing of the burning candles, Cambacères introduced the plaited wicks, which, while burning, become so twisted that the end of the portion of the wick which protrudes from the tallow or stearine is kept just outside the flame, so that it may be consumed to ash by the ambient air. Before the wick can be used in candles it has to be prepared, because unprepared wick leaves by its incomplete combustion a considerable quantity of a carbonaceous residue which greatly impairs the capillary action. When stearine candles were first made it became necessary to impregnate wicks with substances which should promote the combustion, and De Milly found (1830) that boracic and phosphoric acids would answer this purpose, because these acids, while combining with the constituents of the ash of the wick, caused the ash to form at the top of the burning wick a glass bead, which by its weight turned the wick out of the flame, thereby increasing the combustibility. In the French candle factories the wicks to be prepared are put for three consecutive hours into a solution of 1 kilo. of boracic acid in 50 litres of water. The previously plaited wicks are next either wrung out or put into a centrifugal machine to get rid of the first excess of moisture, after which they are dried by being placed in a acketted tinned-iron box, which is heated by means of steam. Some alcohol should be added to the aqueous solution for the purpose of wetting the wicks more perfectly. Payen recommends a pickling liquor for wicks, composed of a solution of 5 to 8 grms. of boracic acid in 1 litre of water, to which 3 to 5 per mille of sulphuric acid is added. In some Austrian stearine candle factories phosphate of ammonia is used to impregnate the wicks; while Dr. Bolley calls attention to the use of a solution of sal-ammoniac at 2° to 3° B. as a cheap pickling for wicks.

Moulding the Candles. The blocks or cakes of stearic acid obtained as described are not sufficiently pure for moulding. The edges of the blocks are often more or less coloured and soft, owing to some oleic acid not having been pressed out, while the surface of the blocks is contaminated with oxide of iron and the hair of the press-bags. In order to purify the blocks or cakes (in this country they frequently weigh from 1½ to 3 cwts.) the edges are pared off and the surface is scraped, the refuse so obtained being again submitted to hot-pressing. The blocks thus treated are next put into tubs lined with lead, and dilute sulphuric acid of 3° B. = 1·020 sp. gr. having been poured over them, the fluid is heated by means of steam, the aim of this operation being to remove oxide of iron and destroy the fibres of the press-bag, and not, as is sometimes stated, to decompose the last traces of stearate of lime, which of course cannot be present. When the action of the sulphuric acid has been continued for a sufficient time, it is run off and the last trace of the acid removed by washing the stearic acid, of course again molten, with boiling water. The molten stearic acid is then clarified by means of a certain quantity of white of egg, which is thoroughly stirred through the molten mass heated to the boiling-point of the water mixed with it. The impurities which become mixed and incorporated with the white of egg settle at the bottom of the vessel. The great tendency of the stearic acid to crystallise in large foliated crystals caused at the commencement of the stearine-candle making business a difficulty, candles of unequal transparency as well as of great brittleness being obtained. The defect was remedied by the addition of a small quantity of arsenious acid, but as this proved detrimental to health (arseniuretted hydrogen as well as some arsenious acid being evolved during the burning of such candles), the use of this acid was abroad prohibited by law, and in England condemned by public opinion. Instead of the use of arsenious acid, some 2 to 6 per cent of white wax has been added to the stearic acid while molten, continually stirring until nearly solidified previous to pouring the stearic acid into the candle-moulds previously heated to the melting-point of the stearine. By the cooling and stirring a kind of fluid-fat paste was obtained which does not crystallise. Now some 20 per cent of paraffin is added to the stearic acid, and its tendency to crystallise altogether suspended.

The candle-moulds are made of an alloy of tin and lead, usually consisting of 20 parts of tin to 10 of lead. The moulds are narrow, somewhat conical tubes, highly polished internally in order to impart a smooth surface to the candles. The wick is fixed in the longitudinal axis of the moulds, being fastened at one end (the top of the finished candle) in a small hole at the bottom of the mould, and at the other end fastened to a funnel, through which the fatty acid is poured into the mould. The shape of the moulds used in the French stearine candle works is exhibited in Fig. 269. *a* is a mould consisting of two parts, viz., the mould proper and the funnel. *b* exhibits these two parts fitted together, and *c* a longitudinal section with the wick inserted, while *d* is the wire hook with which the wick is passed through the mould. For the moulds now generally used one moulding-basin or box is employed to contain thirty moulds. This basin or moulding-box is exhibited in Fig. 270. A D is a large sheet-iron or tinned box in which the moulds are placed. This box is fitted into another of similar shape, B B, which by means of steam is kept at a temperature of 100°. As soon as the moulds are heated to 45°, the box A D is removed from B B, and the molten stearic acid is poured into the moulds. When the moulds and the candles contained have become quite cold, the latter are removed. Now moulding machines are generally employed, so that this operation is performed uninterruptedly, the construction of these machines being such that the reeled wick is drawn through the moulds while the candles remain joined together by a short piece of wick until after the moulding is complete, the candles when cold being taken from the moulds and the wicks cut through to separate them. Cahouet's and Morgane's machines are chiefly used.

Before the stearine candles are pared and polished they are in some works bleached by being exposed to the action of the sun's rays and to dew in open air. The candles are carried to the bleaching-ground by mechanical self-acting means, consisting of a cloth without end, and which is connected with a slightly sloping table, upon which the candles are placed, and caught by the cloth, which is fitted with a series of rounded wooden laths fastened across the cloth, whereby the candles are held in position. For the purpose of exposing the candles to the action of the air they are placed on a frame-work similar to that of a table, instead of the top of which are stretched two textures of lead-wire, each of these textures in a horizontal plane distant from each other about half the height of a candle. The meshes of the upper wire net are so wide that a candle can be passed through it, while the meshes of the lower wire net are narrower. The candles are one by one put into the meshes, the pointed portions of the candles being placed upwards, while the base rests on the lower wire net. In this position the candles are left for some time according to the season of the year. When bleached the candles are pared and polished by machinery.

Tallow Candles. 2. Refined, purified tallow is used for making the dip as well as the moulded tallow candles. The dips are made by the repeated immersion of the wicks in molten tallow. On the small scale this operation is performed in the following manner:—The tallow trough having been filled with molten tallow, the wicks looped on a wooden or thin iron rod are immersed in the tallow. According to the weight it is desired to give to the candles, from sixteen to eighteen wicks are looped on to the dipping-rod, care being taken to place them as much as possible equidistant from each other; this done the wicks are dipped vertically into the molten tallow. At the first dip, when the wicks are to be soaked, the molten tallow should be hot, because hot tallow penetrates more readily into the insterstices of the cotton. After the first dip the dip-rods are placed on the edge of the tallow trough, and next alternately hung over the dripping frame after the somewhat twisted wicks have been put straight again. The dripping frame is simply a wooden frame-work, on the edges of which the dipping-rods rest, while the wicks are suspended over the tallow trough or another suitable vessel. When all the wicks looped on to the dipping-rods have received their first dip, and the tallow in the trough has been so far cooled as to begin to exhibit at the sides of the vessel signs of solidification, the second dip is proceeded with and the operation continued until the candles have assumed the desired thickness. As the lower portion of the candles would become frequently thicker than the upper, this defect is obviated by keeping the lower end of the candle for a moment in the molten tallow, so that the excess adhering to the candle may be molten off

FIG. 269.

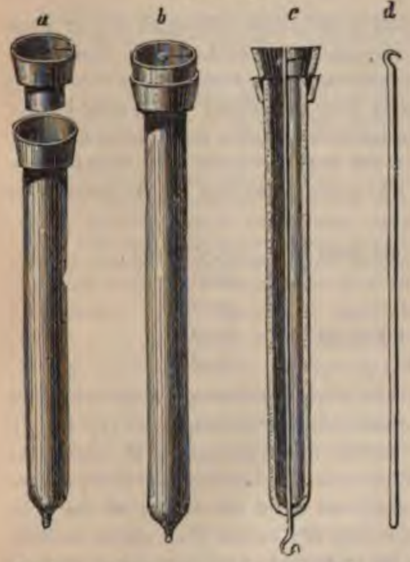
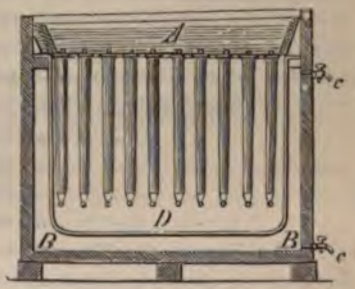


FIG. 270.



again. In order to keep the tallow in the trough at a uniform degree of fluidity it is now and then stirred with a wooden rod. At the last dip the candles are put into the trough at a somewhat greater depth in order to form the upper conical portion. The lower end of the candles exhibits a non-symmetrical cone, which is either cut away or removed by placing the candles for a moment on a copper plate heated by steam and provided with a channel for running off the molten tallow.

Moulded tallow candles are made in a similar manner to stearine candles. The tallow used for the moulded candles is usually of better quality than that used for dip candles, at least on the continent of Europe; not so in England and America, where very highly refined tallow is used for dips by the better class of makers, the thus refined tallow being harder owing to the mode of purifying. What are termed composite candles (unknown on the Continent) are made by precisely the same method as the moulded stearine candles, the wicks also being plaited. Moulded tallow candles have been entirely superseded by composites, excepting that in some of the central parts of Europe, locally moulded tallow candles are here and there made. One of the largest London firms states that the manufacture of candles (almost all moulded, viz., composites, stearine, paraffin, ozokerite, spermaceti), for exportation from this country to all parts of the world, is increasing to such an extent that the candle making business in Russia, Turkey, Greece, Italy, Spain, Portugal, Sweden, and Norway, is becoming rapidly extinct, not being capable to compete on the small scale with the large makers in this country and in France, where, however, the late lamentable events have very seriously interfered with this branch of industry.

Paraffin Candles. Paraffin is obtained from native petroleum (Rangoon oil) or from among the products of the dry distillation of peat, brown coal, lignite, bituminous slates, boghead mineral or ozokerite (a peculiar mineral, wax-like, and yielding paraffin—it occurs in Galicia and Bohemia in large quantities) It is, after having been purified, the substance from which the beautiful paraffin candles are made by precisely the same methods and apparatus as are used and have been described for stearine candles. The paraffin employed for making candles is a mixture of paraffins having different melting-points.

Paraffin obtained from boghead coal	fuses at	45·5° to 52°.
,, ,, ,, brown coal	,,	56·0°
,, ,, ,, peat	,,	46·7°
,, ,, ,, Rangoon oil or tar	,,	61·0°
,, ,, ,, ozokerite	,,	65·5°

As the German paraffin candle makers use almost exclusively a paraffin from brown coal (lignite), and peat, and of a comparatively low melting-point (45° to 53°), stearic acid is added for the purpose of raising the temperature at which the paraffin melts. The quantity of stearic acid (technically stearine) added, depends as much upon the point of fusion of the paraffin as upon the season of the year, summer candles being made with a larger quantity of stearine than winter candles. The quantity of stearine thus added to paraffin amounts to 3 to 15 per cent, while as already mentioned, paraffin to an amount of 15 to 20 per cent is added to stearine candles. A small quantity of stearine is always added to paraffin candles for the purpose of preventing these candles becoming bent while standing in a candlestick.

The first paraffin candles ever made were manufactured by Messrs. Field, of Lambeth, from paraffin extracted from Irish peat, now very many years ago, long before paraffin was seen or known elsewhere than as small specimens in chemical laboratories. Paraffin candles are always moulded, and the moulds are heated to above the melting-point of the paraffin (60°, or better even 70°), in order to prevent the paraffin crystallising. The molten paraffin is heated to about 60° when it is cast into the moulds; these when well filled are left standing for a moment and then cooled by immersion in cold water, whereby the candles suddenly solidify, and are thus prevented becoming crystalline and opaque, instead of transparent as desired. Plaited wicks are used in the paraffin candles, and these wicks are treated with boracic acid. For black paraffin candles the paraffin is heated to nearly its boiling-point with anacardium shells, the resin of which is dissolved by the paraffin, the latter becoming very dark brown, and exhibiting after cooling a black colour, similar to that of coals. These black candles burn without smoke or smell, provided the wick be thin; this is a requisite in all paraffin candles.

Candles from Fatty Acids. We must not neglect to call attention here to a fatty acid, sebacylic acid, $C_{10}H_8O_4$, which might perhaps be used to impart to paraffin and other kinds of candles a higher melting-point. This acid may be obtained by the dry distillation of oleic acid, or better by treating castor oil with a highly concentrated caustic soda solution. In the latter instance, the sebacylic acid is derived from the ricinoleic acid (castor oil is in Latin termed *Oleum Ricini*):—

$$\left.\begin{array}{lr}\text{Ricinoleic acid, } C_{18}H_{34}O_3 & = 298\\ \text{Caustic soda solution, } 2NaOH & = 80\end{array}\right\}\text{ yield }\left\{\begin{array}{lr}\text{Sebacylate of soda, } C_{10}H_{16}Na_2O_4 & = 246\\ \quad(= 184 \text{ fatty acid.}) & \\ \text{Caprylic alcohol, } C_8H_{18}O & = 130\\ \text{Hydrogen, } H_2 & = 2\end{array}\right.$$

$$\overline{378} \qquad\qquad \overline{378}$$

According to these formulæ, 100 parts of castor oil will yield rather more than 81 parts of fatty acid. This fatty acid is no doubt also contained in the products of the distillation of the fatty substances formed by sulphuric acid, the sebacylic acid being then derived from oleic acid. The high melting-point (127°) of sebacylic acid and its ready combustibility render this body a very fit material for being mixed with readily fusible candle materials, and especially with paraffin of low fusion-point (45°). Moreover, this acid will impart to the candles hardness and gloss. As this acid further also prevents the crystallisation of stearic acid, it might be usefully added to such fatty substances as have a great tendency to crystallise; an addition of 1 to 5 per cent of sebacylic acid to the candle materials, renders them as hard as wax. The simultaneous formation of caprylic alcohol, which can be used for varnish and lacquer making, enhances the industrial value of sebacylic acid; still castor oil is too expensive for this purpose, but the purification of sebacylic acid, obtained no matter from what source, is not easy, requiring manipulations which on the large scale would become expensive.

Wax Candles. 4. Wax, or more particularly bees'-wax, is a fatty substance secreted by the bees, and employed by them for the purpose of building the cells in which they preserve the honey. According to the researches of J. Hunter and F. Hubner, it is now generally admitted that the wax-containing particles gathered by the bees from flowers are used exclusively as food for the young brood, while the wax is a product of the animal organism of the bees, and a conversion product of sugar. In order to obtain the wax the bees are either killed or forced from their dwelling by smoke, after which the honey-containing cells or honeycombs are taken from the hive, and the honey eliminated by pressure, or by being allowed to flow out spontaneously. By washing in hot water the wax is purified, and on cooling, the cakes of yellow wax are obtained, the outer dirty crust having been removed by scraping. The crude wax thus obtained exhibits a more or less yellow colour, is soft and readily kneaded at the ordinary temperature of the air, but becomes brittle at a lower temperature; its fracture is granular; specific gravity varies between 0·962 and 0·967; fusion-point between 60° and 62°. While the granular texture of the yellow wax is due to the impurities it contains, it is for that reason as well as for its unsightly colour, not suited for candle-making, and has therefore to undergo bleaching. This is performed in the following manner;—First, the yellow wax is put into a tinned copper cauldron filled with boiling water, to which is added 0·25 per cent of alum, or cream of tartar, or sulphuric acid, and this mixture thoroughly stirred. After a few minutes the liquid is run off into a tub or cask, the impurities are left to settle, while the wax is prevented from solidifying by covering the tub with a lid, and wrapping it up in a woollen blanket. Next the wax is converted into thin ribbon by means of machinery, in order to increase the surface and facilitate the bleaching action of the air and light. The ribbons are placed on pieces of canvas stretched in frames, and these are placed on meadows or grass-plots exposed to the action of the sun and air, and left until the colour has disappeared. In order to bleach the interior, the ribbons are again molten and again converted into ribbons, and this operation repeated until the wax is thoroughly bleached. The bleaching takes, according to circumstances, the state of the weather and the kind of the wax operated upon, from twenty to thirty-five days, for completion. The loss of weight of wax incurred amounts to 2 to 10 per cent. The bleached wax is molten again, passed through strainers, and then moulded into large square cakes or thin circular tablets. As regards the bleaching of wax by artificial means (chemical bleaching) many suggestions have been made, but in practice these leave much to be desired. The application of chlorine and bleaching-powder has the disadvantage that solid and very brittle chlorinated products are formed, and by remaining mixed with the wax impair its combustive quality, and cause candles made of such wax to give off hydrochloric acid. The process of bleaching wax, patented in 1859 by Arthur Smith, by the use of bichromate of potash and moderately dilute sulphuric acid, answers very well in practice; the bleaching is performed in a few hours, and wax by this plan is bleached and purified as perfectly as by exposure to air and light; but the toughness of the wax is somewhat impaired, so that it is not suitable for such purposes as modelling, flower-making, &c. In reference to the chemical properties of wax, John first found wax to be a mixture of two substances differing from each other by their solubility in alcohol; one of these substances, soluble in boiling alcohol, is cerotic acid, $C_{27}H_{54}O_2$ (formerly known as cerin); the other sparingly soluble in alcohol is known as myricin, and consists, according to Brodie, of palmitate of myricile, $C_{46}H_{92}O_2 = C_{16}H_{31}(C_{30}H_{61})O_2$. In addition to these bodies wax contains 4 to 5 per cent of a substance fusing at 28° and named cerolein, to which is due the solidity of wax. The relative proportions of cerotic acid and myricin present in bees'-wax vary considerably, and this variation is the cause of the alteration of the fusion-point observed in different kinds of wax.

Other kinds of Wax. 1. Among the more or less wax-like substances are the following:—Chinese wax, imported in large quantity from China, is derived from a peculiar kind of coccus insect, known entomologically as the *Coccus ceriferus*, which dwells on certain trees, more especially the *Rhus succedanea*, upon which it deposits a wax-like substance, in its physical appearance very similar to spermaceti. This quasi-wax is snow-white, crystalline, brittle, fibrous, and fuses at 82°. When submitted to dry distillation it yields cerotic acid and ceroten, a paraffin-like body. According to Brodie, Chinese wax consists of cerotate of ceryl, $C_{54}H_{108}O_2 = C_{27}H_{53}(C_{27}H_{55})O_2$. 2. Andaquies wax, the product of an insect met with in the regions watered by the Orinoko and Amazon rivers, fuses at 77°, has a sp. gr. of 0·917, and appears to be similar in composition to bees'-wax. 3, Japanese or American wax, met with in the trade in round concavo-convex cakes, covered with a whitish dust. This soft brittle material fuses at 42°, is soluble in boiling alcohol, and is said to consist of palmitine. 4. Carnauba wax, imported from Rio de Janeiro, is said to be the outer coating of the leaves of a kind of palm tree named the *Kopernicia cerifera*; it fuses at 83·5°, and is used on account of its high fusion-point to improve candle-making materials of low fusion-point. 5. Palm wax, obtained from the bark of the *Ceroxylon andicola*, a palm-tree met with on the higher peaks of the Cordilleras. The wax is scraped from the bark, and the scrapings are boiled with water, and the wax thus molten is collected from the surface of the liquid, in which the impurities remain. This kind of wax fuses at 83°—86°, and is very likely identical with the Carnauba wax. 6. The Myrica wax, from the *Myrica cerifera*, is obtained by boiling the fruit of the plant with water. It is imported from some of the Southern States of the Union. The variety of this wax known as Ocuba wax is obtained from the same plant and in the same manner, in the district of Para, Brazil, along the banks of the Amazon river. This wax has an olive-green colour, and fuses at 36° to 48°. It is used in America for making candles. We may add here that of all countries in Europe, if not in the world, Corsica produces the largest quantity of wax. In ancient as well as medieval times, the inhabitants paid their taxes in wax, and supplied 200,000 lbs. annually. Since wax is to honey in quantity as 1 to 15, the Corsicans must have gathered 3,000,000 lbs. of honey.

The Making of Wax Candles. Wax candles are most frequently made by pouring the molten wax on to the wicks. For this purpose the wicks are hung upon frames and covered with metal tags at the ends to keep the wax from covering the cotton in those places; these frames are carried to a heater, where the wax is melted. The frames can turn round, and as they turn a man takes a vessel of wax and pours it first down one, and then the next, and so on. When he has gone once round, if the wax is sufficiently cooled he gives the first wick a second coat, then the third, &c., until they are all of the required thickness. The candles are now rolled on a marble slab or wooden board for the purpose of imparting the proper shape. The conical top is moulded by properly shaped tubes, and the bottoms are cut off and trimmed. The moulding of wax candles is now rarely if ever performed, but if executed, it is done in precisely the same manner as described for stearine and paraffin candles. Wax, however, is not a very suitable material for moulding, in consequence of its shrinking on cooling, as well as its pertinacious adherence to the moulds. The wick for moulded wax candles must be previously soaked with wax in order to prevent the candles becoming as it is termed honey-combed. The wax is molten on a water-bath, and glass moulds are used in preference to metal ones, as well for the smooth surface glass imparts as for the more ready removal of the candles when cold. In order to prevent the breaking of the glass moulds, they are covered with gutta-percha. The large sized altar candles, which often weigh from 15 to 20 kilos., are not made by either of the two methods described, but by hand. The wick, partly made of linen, partly of cotton yarn, is first soaked with wax, or covered with that material cut into long strips, rendered soft and kneadable by the aid of warm water, and next made up to the required thickness by rolling on more wax; or a quantity of wax is rolled by hand into the required shape, and the wick inserted by cutting a longitudinal channel in the mass of wax into which the wick is placed. The channel is filled up with wax and the candle finished by rolling. Very recently (1870) Messrs. Riess have constructed a press for making wax candles. The arrangement of this machine seems to be somewhat similar to the press used for making continuous lengths of lead and block-tin pipes. This wax candle press is heated by steam so as to render the wax soft. The wick is inserted into the wax in such a manner that it is concentrically surrounded with wax when ejected from the spout of the cylinder of the press, thus forming a continuous candle, which is cut up into lengths.

The wax tapers of various thickness are made by a method of which the following is an outline:—In the first place, these tapers are not made of pure wax, but of wax and tallow mixed, in order to impart flexibility; while for coloured wax resin and turpentine are added to the tallow. The wick of the tapers should be very uniform, and the strands of yarn intended for this purpose are reeled on a cylinder or drum placed at one end of the workshop, while at the other end is placed a similar drum. Between these drums is placed a shallow copper pan, which can be kept warm by means either of steam or a charcoal fire. This vessel is filled with the molten wax, and provided with a hook at the bottom, below or through the opening of which the wick is drawn. At the edge of the pan a draw-iron is fixed, provided with circular, somewhat conical, apertures of different size, arranged in the same way as those described (see p. 25) for wire-drawing. The wick is drawn through the wax, put under the hook, and through the aperture of the drawing-iron, and next reeled on the other cylinder or drum, which is very slowly turned round in order to give the wax time to solidify. When all the wick has been thus coated with wax, the taper is, when required to be rendered thicker, drawn a second, and even a third and fourth, time through the wax, and a larger-sized aperture of the drawing-iron. The endless taper thus formed is cut up into the requisite lengths.

Bees'-wax is used for many minor purposes, as is well known. Amongst them, as of interest, may be noted its selection by the British Government for a lubricating material for small-arm cartridges and also for breech-loading cannon. This is due partly to its power of resisting oxidation, and its consequent freedom from corrosive action upon metal surfaces (lead, &c.), and partly to its peculiar action as a lubricating material, by producing an extremely smooth surface upon the bore of the arm as it is swept through upon the discharge. It also prevents particles of paper or powder residue from attaching themselves to the metal, and thus is the best anti-fouling agent known.

Sperm or Spermaceti Candles. Spermaceti is the solid portion of the oil of the sperm whale, *Physeter macrocephalus*, a cetacean belonging to the mammalia, and living in some of the seas of the southern hemisphere of our globe. The spermaceti is obtained from the oil by filtration, and is subsequently hardened and whitened by pressure, and refining with a weak alkaline ley. In some cases a very large and full-grown sperm whale may yield 100 cwts. of sperm oil, containing from 30 to 60 cwts. of spermaceti. This material as met with in commerce is a white, mother-of-pearl like, glossy, foliated, crystalline, semi-transparent substance, fatty, and lubricating to the touch, of sp. gr. = 0·943, fusing at 43°, and distilling unaltered at 360°. It is soluble in about 30 parts of boiling alcohol, becomes yellow by exposure to air, and may be pulverised. According to Mr. Smith and Dr. Stenhouse, spermaceti consists of palmitate of cetyl, $C_{34}H_{64}O_2 = C_{16}H_{31}(C_{16}H_{33})O_2$; but according to Heintz (1851), spermaceti is a combination of cetyl with stearic, palmitic, myristic, cocinic, and cetinic acids. Spermaceti candles are made extensively, if not exclusively, in England, where they were first manufactured about 1770. These candles have always been greatly prized for their transparent whiteness, high illuminating power, and regular burning; and notwithstanding their costliness, are largely used and exported to British India. In order to check the great tendency of spermaceti to crystallise, 5 to 10 per cent of white wax or a little paraffin is added to the fused mass intended to be moulded into candles, by a process exactly similar to that already described for stearine candles.

Glycerine. Glycerine, $C_3H_8O_3$ (as triatomic alcohol, $\left.\begin{matrix}C_3H_5\\H_3\end{matrix}\right\}O_3$, or $C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right)$, is present in the shape of glycerides in combination with solid and fluid fatty acid to an amount of 8 to 9 per cent, and may be separated by treatment with bases (potash, soda, lime, baryta, oxide of lead), or with acids (sulphuric acid), and certain chlorides (chloride of zinc), also by means of superheated steam, or very hot water without the formation of steam, in closed vessels. Glycerine is also formed as a constant product by the alcoholic fermentation of dextrose, levulose, and lactose. According to Pasteur's researches, the quantity of glycerine thus formed amounts to about 3 per cent of the weight of the sugar. Glycerine was first discovered by Scheele whilst engaged in preparing lead plaster. Industrially, glycerine has been used for only twenty-five years, in consequence of the large quantity of glycerine obtained as a by-product in the manufacture of soap as well as of stearine candles. The vinasse of the potato, and molasses from beet-root sugar distillation, and likewise the residue of the distillation of wine, vinasse proper, as carried on in the South of France, contain large quantities of glycerine.

As regards the preparation of glycerine on the large scale, it is mainly a question of purification of the glycerine obtained in the industrial preparation of the stearic acid from neutral fats above described. When the lime saponification process is used, the glycerine remains dissolved in the water after the separation of the insoluble lime-soap. The lime also dissolved having been eliminated by either sulphuric or preferably oxalic acid, the evaporation of the liquid to the consistency of a syrup will yield a glycerine pure enough for many technical purposes. When the decomposition, or rather dissociation, of the neutral fats is effected by means of superheated steam, the glycerine and fatty acids (see p. 634) are both obtained in pure state, provided the heat be kept at or below 310°, because otherwise a portion of the glycerine is decomposed with evolution of vapours of acroleine. The fact that, when fats are saponified with sulphuric acid, the sulpho-glyceric acid in aqueous solution yields readily by evaporation glycerine and sulphuric acid, may be applied for the preparation of glycerine. The soap boiler's mother-liquor, now the most important source of crude glycerine, may be made available for its production, according to Reynold's patent, in the following manner:—The mother-liquor is first concentrated by evaporation; the saline matter which is thereby gradually separated being removed from time to time. When the fluid is sufficiently concentrated—ascertained by the boiling-point having risen to 116°—it is transferred to a still, and the glycerine distilled off by means of superheated steam carried into the still. The distillate is next concentrated and brought to the consistency of a syrup in a vacuum pan.

According to the researches of A. Metz (1870):—

A sp. gr.	(at 17·5°) of	1·261	corresponds	to	100	per cent	of anhydrous	glycerine.
,,	,,	1·240	,,	,,	94	,,	,,	,,
,,	,,	1·232	,,	,,	90	,,	,,	,,
,,	,,	1·206	,,	,,	80	,,	,,	,,
,,	,,	1·179	,,	,,	70	,,	,,	,,
,,	,,	1·153	,,	,,	60	,,	,,	,,
,,	,,	1·125	,,	,,	50	,,	,,	,,
,,	,,	1·117	,,	,,	45	,,	,,	,,
,,	,,	1·099	,,	,,	40	,,	,,	,,
,,	,,	1·073	,,	,,	30	,,	,,	,,
,,	,,	1·048	,,	,,	20	,,	,,	,,
,,	,,	1·024	,,	,,	10	,,	,,	,,

Glycerine has become largely employed owing to its oily consistency, also to the fact that at ordinary temperatures it is fluid, and does not freeze when quite concentrated even at −40°;* further to its stability, its pleasant sweet taste when quite pure, its harmlessness, its great solvent power for many substances, and, lastly, to its low price.

Among the many applications of glycerine are the following:—For keeping clay moist for modelling purposes; for preventing mustard from drying up; for keeping snuff damp; preserving fruit; sweetening liqueurs; and for the same purpose for wine, beer, and malt extracts. Glycerine is also useful as a lubricating material for some kinds of machinery, more especially watch and chronometer works, because it is not altered by contact with air, does not become thick at a low temperature, and does not attack such metals as copper, brass, &c. Glycerine is used in the making of copying inks, and of a great many cosmetics. In order to render printing ink soluble in water—its insolubility is, however, its greatest advantage—it has been proposed to use glycerine for its preparation instead of linseed oil. Glycerine is an excellent solvent for many substances, including the tar-colours (aniline blue, cyanine, aniline violet) and alizarine. In order to render paper soft and pliable glycerine is added to the pulp. To the quantity of pulp required for making 100 kilos. of dry paper, 5 kilos. of glycerine, sp. gr. 1·18, are sufficient. It is not out of place here to mention the following useful weavers' glue or dressing, composed of—Dextrine, 5 parts; glycerine, 12 parts; sulphate of alumina, 1 part; and water, 30 parts. By the use of this mixture the weaving of muslins need not be—as was formerly the case—carried on in damp darkened cellars, but may be performed in well-aired and well-lighted rooms. It is said that leather driving belts, made as usual of weakly tanned leather, when kept in glycerine for twenty-four hours, are not so liable to fray. A glycerine solution is now largely used instead of water for the purpose of filling gas-meters, as such a solution does not freeze in winter nor evaporate in summer. Santi uses glycerine for the compasses on board screw-steamers, in order to protect the inner compass box against the vibrations caused by the motion of the propeller. It is impossible to enter here into minute details on the use of glycerine; suffice it to observe further that it is employed for preserving anatomical preparations, for rendering wooden casks impervious to petroleum and other oils; for the preparation of artificial oil of mustard or sulpho-cyan-allyl, made by treating glycerine with iodide of phosphorus, whereby iodide of allyl is formed, which on being dissolved in alcohol, and next distilled with sulphocyanide of potassium, yields sulpho-cyan-allyl. When glycerine is treated with very concentrated nitric acid or with a mixture of strong sulphuric and nitric acids, it is converted into nitro-glycerine (trinitrine or glyceryl nitrate) (see p. 158), largely used for various purposes, the preparation of dualine and dynamite, &c. A mixture of finely powdered litharge and very concentrated glycerine made into a paste forms a rapidly hardening cement, especially useful as a cover for the corks or bungs of vessels containing such fluids as benzol, essential oils, benzoline, petroleum, &c., the cement being impermeable to these liquids.

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* The freezing of glycerine, observed in 1867, by Mr. W. Crookes, in London; by Sarg, at Vienna; and Dr. Wöhler, at Göttingen, proves, however, that under certain conditions, and while being transported from one place to another, glycerine may become solid even at a temperature not so low as the freezing-point of mercury.

II. *Illumination by Means of Lamps.*

Illumination with Fluid Substances. The fluid substances in use as illuminating materials are either:—*a*. Fixed, or fatty oils. *b*. Volatile oils, which again are either essential oils, as, for instance, camphine; or products obtained from tar, as photogen and solar oil; or, finally, native, as petroleum. Among the fixed or fatty oils, rape-seed oil, colza oil, olive oil, fish oil, and the dry papaver-seed or poppy-seed oil, are chiefly used.

Purifying or Refining the Oils. In order to refine these oils so as to render them more suitable for combustion in lamps, they are treated with about 2 per cent of their weight of strong sulphuric acid, or with a concentrated solution of chloride of zinc. These substances do not act upon the oil, but destroy or coagulate any impurities, as mucilaginous and colouring matters, present. The acid or chloride of zinc is removed by washing with water, after which the oil is filtered, and in order to remove any mechanically adhering water, it is kept for a considerable time at a temperature of about 100°, being heated by means of steam circulating in pipes fitted in the tanks. Now oil is frequently extracted from the seeds by means of sulphide of carbon (see p. 199). The oils which serve for the purposes of illumination are termed lamp-oils The introduction of paraffin and petroleum oils has caused a very considerably decreased consumption of the fixed fatty oils.

Lamps. Lamps were known and used even in remote antiquity, and were invented, it is believed, by the Egyptians. While it cannot be denied that as regards outward form the lamps of the ancients were graceful, their technical construction was rude, and remained so—not taking into account some minor improvements made in the seventeenth and eighteenth centuries, among which improvements are the introduction of the glass cylinders by the Parisian apothecary Quinquet, and the invention of the hollow and circular burner by Argand, 1786—until chemistry discovered a sound theory of combustion and illumination, and until physicial science ascertained the principles of the supply of oil and means of estimating the illuminating power of the flame of lamps, and further until the refining of oil supplied a purer and more fluid illuminating material. A still greater step to improvement in light obtained from lamps was the discovery of the petroleum and paraffin oils and the construction of lamps suitable for their combustion. These oils have now become of general use wherever gas is not obtainable. In passing, it may be observed that in no country is gas so extensively made on the small scale as in Scotland, where farm-houses, country seats, and other dwellings, not conveniently situated near to public gas-works, are very generally provided with small gas-works, in which the excellent Cannel coal of the country is employed, yielding a very pure and highly illuminating gas at a reasonable cost, and with the advantage that gas is allowed by the insurance companies as light in stables and other places where readily inflammable materials are kept, while lamp and candle lights are absolutely prohibited in such places, for fear of causing fire. Some of the many inventions and improvements of oil lamps made during the last forty-five to thirty years are quite forgotten; the moderator colza lamp has been nearly superseded by improved paraffin and petroleum oil lamps, and as we do not treat in this work on the history of technology, but on technology as now developed, we cannot enter into any further historical details, but proceed with our subject.

Viewing lamps generally, we observe the same parts as in a candle, viz., the illuminating material and the wick. As regards the illuminating material, it is in lamps as well as in candles fluid, the difference consisting in that with candles the fatty material is molten near the end of the wick, a cup of molten fat being formed, while with lamps the illuminating material is fluid at the ordinary temperature, and therefore kept in a vessel or reservoir from which the wick is uninterruptedly and as uniformly as possible supplied. The differences observed in the construction of the various kinds of lamps depend partly upon the illuminating material employed (colza oil, petroleum oil, sperm oil, &c.); partly upon the shape of the wick and upon the mode of supplying air to the flame, either with or without a glass chimney; further, upon the shape of the oil reservoir and its position in reference to the wick; and finally and chiefly, upon the method and means by which the illuminating material is carried to that portion of the wick where the combustion is intended to take place; that is to say, whether the illuminating material is only absorbed by the capillary action of the cotton wick, or whether this action is aided by hydrostatic or mechanical means.

Colza oil and mineral oil—be the latter obtained from the tar yielded by the dry distillation of certain kinds of coal or peat, or be it derived from native petroleum—differ from each other as regards their properties as illuminating materials in the following particulars:—1. Colza oil is not volatile at the ordinary temperature, and not even when heated to above 100°. It is hence devoid of smell, and is not by itself ignitable unless it be first heated to a such a high temperature (about 200°) as to give off products of dry distillation—in fact, become decomposed and converted into oil-gas. The mineral oil, even that kind which is termed odourless, possesses some odour, and loses in weight or is gradually volatilised by exposure to air. At a higher temperature it is volatilised and can be distilled over unaltered, while at a still more elevated temperature it is nearly all converted into illuminating gas. 2. Colza oil consists of carbon, hydrogen, and oxygen, according to the formula

$C_{18}H_{12}O_2$. In the dry distillation which this oil undergoes in the wick just below the flame it is converted into elayl gas and carbonic acid:—

$$\text{Colza oil, } 2C_{10}H_{18}O_2=340\text{, yield}\begin{cases}9\text{ molecules of elayl gas, } 9C_2H_4 & =252\\ 2\quad\text{,,}\qquad\text{,, carbonic acid, } 2CO_2 & =\underline{\ \ 88}\end{cases}$$

$$340$$

consequently 25·8 per cent of the colza oil becoming carbonic acid does not contribute anything to the illuminating power of the flame, but deprives the half of the volume of the elayl gas of its illuminating power. Refined colza oil burns in well-constructed lamps very completely, yielding only the odourless products of combustion, viz., carbonic acid and water. 3. Petroleum oils are mixtures of different hydrocarbons, very probably of the higher members of that homologous series of which marsh gas is the primary. Petroleum oil begins to boil at 250°, and is at a higher temperature decomposed, yielding gaseous products, marsh gas and elayl gas, and soot, or unburned carbonaceous matter. The quantity of carbon contained in petroleum oil is far larger than that contained in colza oil; hence the former when burning in contact with air and without a glass chimney exhibits a sooty flame, but this changes at once into a very bright flame when by the addition of a glass chimney the increased draught of air causes the complete combustion of the excess of carbon. While colza oil only reaches the flame in the state of gas, the petroleum oils come into the flame as vapour, and the construction of the petroleum oil lamps ought to be so contrived that the combustion be as complete as possible in order to prevent any disagreeably odorous vapours or gaseous matters escaping unconsumed. As regards accidents from fire, petroleum or paraffin oil lamps are, with proper precautions and good quality of oil, not attended with greater danger than that of the use of colza oil. 4. As is well known, colza oil is a fatty lubricating oil, while paraffin or petroleum is not so: in consequence of this difference the former may be used in lamps in which the oil is carried to the wick by mechanical means—either by clockwork or spiral springs acting upon one or more more pistons, as in the Carcel and moderator lamps. Because the fatty nature of colza oil as well as its lubricating property keeps the packing of the pistons oil-tight as well as lubricated, it is clear that the paraffin oils cannot be used in such lamps.

Independently of the illuminating material, the construction of a normal lamp should be such, that (1) it yields a maximum of light uniformly for a definite time (three to eight hours). This condition, a consequence of the complete and equal combustion of the illuminating material, can only result from (α) the use of a purified illuminating material; (β) the use of a wick of uniform thickness and structure; (γ) the uniform supply of illuminating material to the flame; (δ) by sufficiently strong heat at the point where the combustion takes place, so that the conversion of the illuminating material into gases may be complete; (ϵ) by the regulation of the supply and access of air. Too small a supply of air often gives rise to a sooty flame, while too large a supply causes a lowering of the temperature of the flame, and hence also separation of soot and formation of odorous products of incomplete combustion; and even if these results do not occur and a complete combustion obtains, too large a supply of air impairs considerably the illuminating power of the flame; (ζ) the means of regulating the size of the flame must be perfect. 2. The lamps ought to be so constructed that the light evolved be not wasted. The well-known reflectors and lamp caps aid the illumination greatly

The reservoir for the oil should be in the first place so situated that its shadow falls on some unimportant part of the field to be illuminated; and secondly, so arranged that the point of gravitation of the lamp be maintained.

Various Kinds of Lamps. Taking the manner of conveying the illuminating material by means of the wick to the flame as a basis for the division of lamps into various kinds, we distinguish the following:—

1. Suction lamps, in which the oil is simply sucked up by the capillary action of the cotton wick from the reservoir. According to the situation of the oil reservoir with reference to the wick, suction lamps can be subdivided into:—α. Those in which the oil reservoir is placed at about equal height with the flame of the burning wick. β. Lamps in which the oil reservoir is placed higher than the burner. These lamps have a detachable oil reservoir, which, having been filled, is inverted into a fixed vessel, an arrangement common in reading-lamps for burning colza oil. 2. Pressure lamps, in which in addition to the capillarity of the wick, mechanical or physical means are employed for the purpose of forcing the illuminating material to the wick. In this variety the oil reservoir is placed at the foot of the lamp. According to the method of forcing the oil to the wick, pressure lamps are:—α. Aërostatic, in which the principle is that of Hero's fountain; into the closed oil reservoir air is forced, and this while trying to make equilibrium with the outer air, presses upon the oil and forces it upwards through a tube to the burner. β. Hydrostatic lamps, based upon the principle of the communicating tubes, in which the heights of fluids of different specific gravity making equilibrium together stands in the inverse relation to their specific gravity. The fluid which has to make equilibrium with the oil and force it up towards the cotton wick should be specifically heavier than the oil. γ. Statical lamps, in which the oil is forced from the reservoir at the foot of the lamp to the burner by the pressure either of the weight of a solid body (for instance, a leaden weight), or by the direct weight-pressure of a piston moving downwards in the oil reservoir. δ. Mechanical lamps, in which the oil contained in the reservoir is forced upwards to the burner either (*a*) by means of pumps set in motion by wheelwork similar to that of a large watch (Carcel lamps with clockwork), or (*b*) by the pressure of a spiral spring acting upon a solid piston (moderateur lamps). In the mechanical lamps the oil is carried to the wicks in larger quantity than is required for the momentary consumption; this excess of oil returns continually to the oil reservoir. The lamps here alluded to are only suited to burn colza oil, and we ought to observe that those mentioned under α, β, and γ, are obsolete, for the very good reason that they have been superseded by better and more simple contrivances; this applies also to the clockwork lamps which were, even when well made, very liable to get out of order and required very pure oil to work well. 3. The lamps for burning the paraffin and petroleum oils are all simple suction lamps, the reservoir being placed under the wick and in its axial prolongation. The lower specific gravity and the greater fluidity of the oils greatly aid the capillary action of the wick, and renders all pressure apparatus superfluous. The so-called benzoline sponge-lamps also belong to the category of suction lamps, the very volatile and highly combustible benzoline (obtained from the crude petroleum) being absorbed by the sponge, more commonly cotton waste or tow, and thence slowly carried by capillary action into the wick.

Suction Lamps. 1. To this kind belong all the lamps in which the oil is simply carried to the flame by the capillary action of the cotton wick, the oil reservoir being placed somewhat below the burning end of the wick. According to the situation of the oil reservoir in reference to the wick, suction lamps can be divided into (*a*), those in which the oil reservoir is placed nearly at the same height as the burning wick. Here we have to observe the two following conditions, viz.:—(*a*) the burning wick is placed in the oil reservoir itself, as may be observed in the kitchen lamp and antique lamp; or (*b*), the oil reservoir and burner are separated from each other, the reservoir being placed by the side of the burner, or, as is the case in the ring lamps, at the circumference of the burner, which is in the centre. β. Those lamps, the oil reservoir of which is placed higher than the burner, as, for instance, in the so-called reading lamp.

Among the suction lamps are the following:—In the antique lamp, Fig. 271, the wick, a skein of cotton, is placed in an open or closed oil vessel, the burning end of the wick simply protruding from the spout. This kind of lamp is technically very imperfect, because, in the first place, the wick has to suck up the oil, when the level of that fluid gradually sinks by the burning of the lamp, to a height far too great for its capillary power; hence the flame will by lack of sufficient oil become gradually more and more lurid, and at last extinguished altogether before all the oil is consumed. In consequence of the thickness of the wick the combustion is incomplete, owing to want of sufficient access of air, the lamp thus burning with a sooty flame; while the body of the lamp throws a great shadow. This last defect is less marked in a kind of kitchen lamp, exhibited in lateral projection in Fig. 272, and viewed in plan in Fig. 273, as by means of the spout the distance between the oil reservoir and the flame is increased, or, in other words, the angle, *c a b*, rendered more acute. The so-called Worm's lamp, Figs. 274 and 275, in former days much used in the Rhine provinces, should be noted on account of the shape of the wick, *t*, which is composed of a flat woven cotton band, instead of a skein of cotton yarn, and thus the access of air to all parts of the wick is so regulated that complete combustion of the oil takes place. The wick is put into the wick-holder, *c*, which is soldered to the ring, *d*, loosely fixed on the rim of the glass globe, which serves as an oil reservoir. By means of the rackwork and pinion, *e* and *e'*, the wick can be turned upwards and downwards, and the flame thus regulated. The part *a* is placed in a candlestick or in any other suitable stand. A glass and globe may be placed over and around the flame. Although this lamp is an improvement on the old-fashioned kitchen lamp, it has many defects.

FIG. 271.

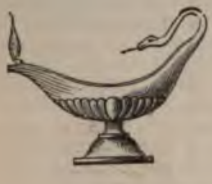


FIG. 272.

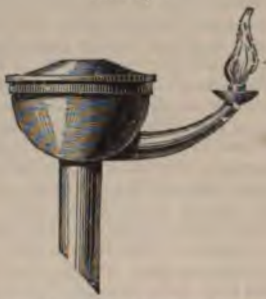


FIG. 273.

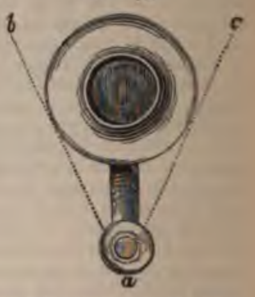


FIG. 274.

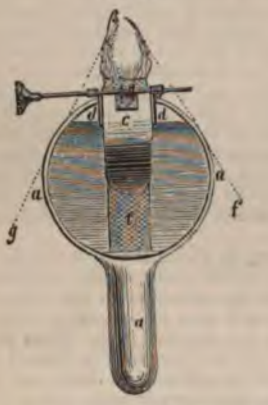
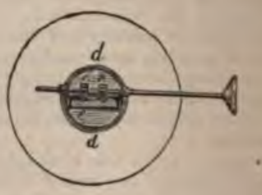
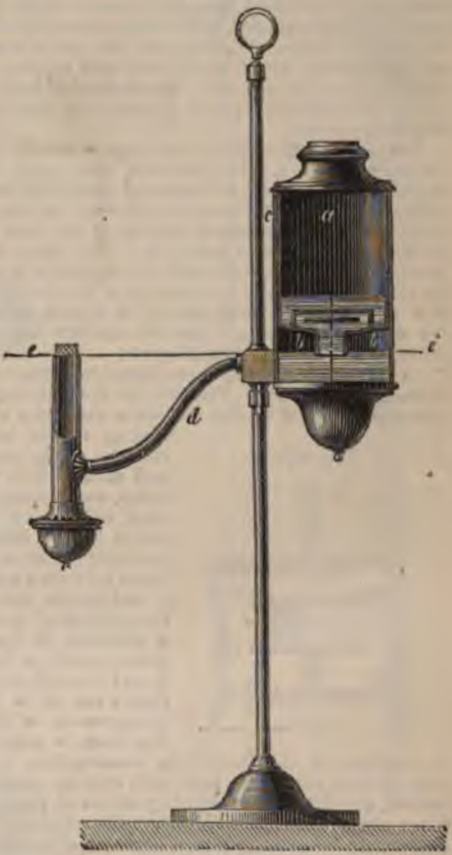


FIG. 275.



The Lamp with Constant Oil Level. In order to obviate the constant decrease in the intensity of the light as the level of the oil sinks by its consumption, as happens in the lamps already described, it is simply necessary to keep the oil in the burner as much as possible at the same height. This can be effected in suction lamps by placing the oil reservoir higher than the burner, but in doing this it becomes necessary so to arrange the construction of the lamp that the oil be gradually carried to the wick in such quantity as is required for its proper burning. This is practically carried into effect as exhibited in Fig. 276, which shows in vertical section a kind of lamp in England known as a reading lamp. The oil reservoir of this lamp is a movable vessel, *a*, of tinned iron, and closed by means of a valve, which when the vessel is placed vertically, as exhibited in the cut, leaves the neck or mouth of the oil flask open in a downward direction, so as to admit of the oil running into the space *bb*; but as soon as the oil has risen to the level, *ee'*, the fluid acts as a hydraulic valve, and no more oil can flow out of *a* until by the burning of the lamp the level has been lowered. The tube *d* carries the oil to the wick-holder; while at *c* a small hole is made for the purpose of giving free access of air to the space between the sides of the vessel *a* and the cylindrical box in which it is placed. When more oil might flow to the wick of this kind of lamp than can be burnt in a given time the flame is extinguished, but, as usually constructed, these lamps, unless they be tilted, or exposed to a very warm atmosphere (in which case owing to the expansion of the air in the vessel *a* the oil is forced out of it) answer the purpose very well, giving when burnt with suitable wicks and well-refined colza oil a good light, but less intense than that obtainable from the better kinds of paraffin oil lamps.

FIG. 276.



Pressure Lamps. 2. These are distinguished from suction lamps by the mode in which the oil reservoir is situated in reference to the burner, the former being not placed on a level with or higher than the latter but below it, the place assigned to the reservoir being the foot of the lamp; and as the capillary action of the wick is not sufficient to enable it to suck the oil upwards to so great a height, an arrangement is required to lift the oil towards the wick, while any excess of oil above that which the flame at the wick is capable of consuming trickles downwards, and is either conducted into the oil reservoir or collected in a separate vessel. The pressure lamps are certainly, as far as colza oil lamps are concerned, the best in every respect; but the different varieties of these lamps to be here noticed have been superseded by the moderateur.

According to the contrivance by means of which the oil in pressure lamps is forced up to the wick, we distinguish:—

a. Aërostatical Lamps.—In these lamps the principle of Hero's fountain is employed. Air is forced into the closed oil reservoir, and this air while trying to gain its equilibrium with the outer air, forces the oil through a very narrow tube upwards to the burner. These lamps have, owing to great complicity of construction, difficulty of management, and of filling with oil, never been of any real practical use.

β. In the hydrostatic lamps, also now obsolete, though in use in France in the earlier part of this century, the oil is forced to the burner by the pressure of a column of liquid upon the oil. The physical principle involved is, that of the two vessels or tubes communicating with each other, and filled with liquids of different specific gravity, the height of these fluids is inversely as the specific gravities of the fluids. The fluid which has to make equilibrium with the oil ought of course to be specifically heavier than the oil, and ought neither to act injuriously upon the metal of which the lamp is made nor upon the oil; while the liquid should not freeze very readily. Mercury, solution of common salt, molasses, solutions of chloride of calcium, and similar liquids, have been proposed as fluids to act in the manner alluded to.

γ. *Statical Lamps.*—In these lamps the oil contained in the reservoir at the foot of the lamp is either forced up to the burner by the pressure of a solid body exerted upon the oil, or by the pressure of a piston, acting directly and by its own weight, forcing the oil upwards through a narrow tube. In the first instance the oil is put into a bag made of any impermeable and sufficiently pliable material—leather, caoutchouc, or waxed silk, for instance—and this bag is placed in a reservoir, and next a weight is made to press upon the bag, to which is fitted a small tube communicating with the burner. The second arrangement with the piston was the forerunner of the mechanical lamps; but as statical lamps are no longer made further details are unnecessary.

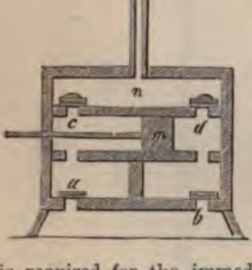
Mechanical Lamps. δ. These lamps are fitted with a mechanical contrivance by the aid of which the oil is forced from the reservoir in the foot of the lamp to the burner, the quantity of oil thus supplied to the latter exceeding the requirements at any given moment of the burning flame. While in all the lamps mentioned the contents of the burner is a constant column of oil, which decreases steadily from the top downwards, or is renewed from time to time, the oil in the mechanical lamps is a constantly flowing stream, which yields the wick the requisite quantity for combustion, while the excess flows downwards into the reservoir.

Two kinds of mechanical lamps are especially noteworthy, viz.:—

Clockwork Lamp. 1. The clockwork lamp, pump lamp, Carcel lamp, invented in 1800, by the lamp maker Carcel, at Paris, and afterwards improved upon. The pump or pumps—for in the better kinds there are two, unless the single pump is double acting—which forces the oil from the reservoir in the foot of the lamp is moved by clockwork, provided with a strong spring which is wound up. The pump is a combination of suction- and force-pump; in some lamps of this kind, instead of a pump an Archimedean screw is employed for the same purpose. In the socket of the clockwork the oil reservoir and pump are placed. The tube through which the oil is forced upwards to the burner is carried through the shaft of the lamp. The oil reservoir and the clockwork are separated from each other by a horizontal metallic plate.

An apparatus of simple construction often employed in the Carcel lamp is shown in section in Fig. 277. The body of the lamp forms the cylinder, in which the horizontal piston *m* is moved to and fro, while the space *n* above it is connected with the oil pipe leading to the burner. The space below the body or cylinder of the pump is connected with the oil reservoir, and divided into two compartments by means of a partition, and further provided with two valves, made either of oiled silk or of gold-beaters' skin. When the piston moves in the direction from *d* to *c*, oil enters from the reservoir through *b*, while the oil then present in the space between *c a* and *m*, is forced through *c* into the space *n*, and thence into the oil pipe. The space *n* serves also the purpose of an air vessel, for the compressed air acts as a regulator to the constant flow of the oil. When the piston moves in the direction from *c* to *b*, oil enters through *a*, and through *d* into *n*. The clockwork which moves the piston rod of *m* is placed below the oil reservoir. The arrangement of the pump is such that the burner of the lamp is supplied with a larger quantity of oil than is required for the immediate consumption of the flame, the result being that the wick and the burner are kept cool, and the carbonisation of the wick at the flame is prevented, and thereby the capillary action of the cotton left unimpaired. The excess of oil flows again into the reservoir. The clockwork of these lamps requires winding up about once in twelve to fifteen hours; and for burning seven to eight hours, the action is so very uniform that a light of equal intensity is maintained for that time. Some of these lamps are fitted with an external knob, which can be used for the purpose of stopping the clockwork by arresting the motion of the regulating wings.

FIG. 277.



Moderateur, or Moderator Lamp. 2. This lamp was invented in 1837 by Franchot, and as it is more simple, less liable to get out of order, and is cheaper than the clockwork lamp, it has in a great measure superseded the use of the latter. The essential part of this lamp is a large, well-packed piston, which resting on the oil contained in the reservoir, is forced downwards by means of a spiral spring, the oil finding no outlet but through a small opening, into which is inserted a narrow tube leading to the burner. A moderateur lamp is exhibited in Fig. 278, the upper part of the cut being a front, the lower a sectional view. The oil reservoir is placed in the hollow body of the lamp, made of metal; this reservoir serves also as pump body or cylinder for the piston A, made of a metallic disc, fitted with a leather rim as packing, and also acting as a valve. To the piston is fitted the rod B, which through nearly its entire length is provided with teeth, biting in those of the small wheel, D, forming a rack and wheel-work contrivance, which admits of drawing the piston upwards by turning the handle of D. When thus wound up the expansion of the spiral spring which is held at E forces the piston downwards. When the reservoir is not filled with oil, the piston rests on the bottom of the vessel; and when oil is poured into the cup of the lamp, it flows downwards into the reservoir and on to the upper surface of the piston: if this is next moved upwards or wound up, there is a vacuum formed below it, and the atmospheric air pressing upon the oil forces it downwards by reason of the flexibility of the leather packing acting as a valve, until all the oil is below the piston and the latter fully wound up, when the oil forces the leather packing so tightly against the sides of the reservoir that there is no way of escape but by the tube C, which communicates with the burner. The spring is very accurately adjusted, and its expansion regulated to the bulk of oil which is consumed, so that the wick is properly supplied. After the lapse of some hours the lamp has to be wound up again. In order to prevent the oil passing through the tube C in too large a quantity at once and being forced out of the burner as a jet, there

FIG. 278.

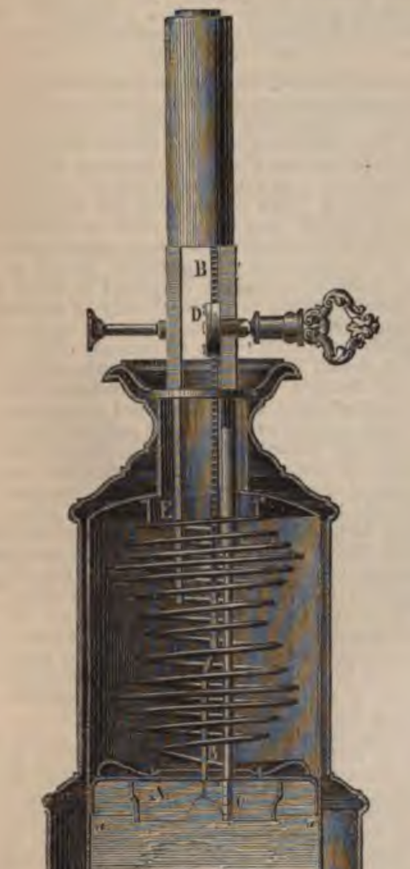


FIG. 279.

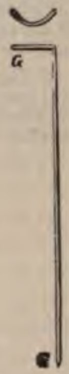
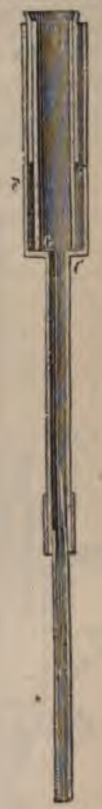


FIG. 280.

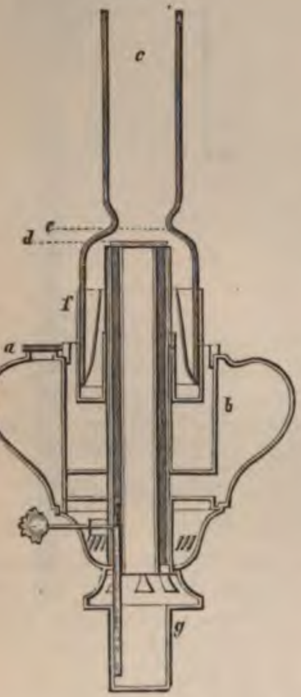


is brought into play a contrivance which is technically termed the moderateur, consisting of (Figs. 279 and 280) a peculiarly bent wire, G, which is placed in the tube C, and is soldered to the inner tube of the lower part of the burner. The lower and movable portion of the tube C is, when the piston is fully wound up, so placed that G fits and dips into C, while, when the piston moves downwards, C is also lowered, and not partly plugged by G. By this arrangement the flow of the oil is rendered uniform and independent of the greater force of expansion exerted by the spiral spring when the lamp has been fully wound up. To some of these lamps an arrangement has been fitted, consisting of a dial and hand, exhibiting externally the position of the piston, so that it may be seen when the lamp again requires to be wound up, and in some cases an alarum has been added for the purpose of giving audible warning when the operation is required. With good colza or sperm oil an excellent light is obtainable, while the machinery is not very liable to get out of order.

Petroleum Oil and Paraffin Oil Lamps.

3. The fluids commonly termed paraffin or petroleum oils, and also known as kerosen, photogen, pyrogen, &c., are always burnt in suction lamps, the oil reservoir being placed either below or by the side of the wick. Mechanical lamps, such as the moderateur lamp, for instance, cannot be used for petroleum oils, because these oils do not lubricate the leather of the piston. As the mineral oils are not viscous, the capillary tubes of the wick can more readily suck up the oil from the reservoir, so that by the lowering of the level of the fluid a loss of intensity in the light is hardly perceptible. Owing to the large quantity of carbon contained in these oils, a smokeless flame is produced only by a powerful current of air, which is obtained partly by the glass chimney and partly by the adjustment of the wick, which should project very slightly above the rim of the burner; while in the paraffin oil lamps provided with flat wicks the object is promoted by the brass cap put over the flame and provided with an opening, below which the admixture of air and vapours of the oil takes place, and also a strong current of air called forth to aid the combustion. In reality the petroleum and paraffin oil lamps are vapour lamps; that is to say, the vapours of these liquids yield the luminous flame, not the gases resulting from the decomposition of the oil, as obtains in the case of colza oil and candles. In order to guard against the possibility of an explosion, the paraffin oil lamps are all so contrived that the fluid contained in the reservoir does not become heated, and for this purpose the current of air which sustains the combustion is made to cool the burner.

FIG. 281.



Among the many paraffin oil lamps one of the best is that of Ditmar, at Vienna. This lamp, Fig. 281, consists of a metal oil reservoir, *b*, which surrounds the wick tube and is connected with that tube by means of a horizontal tube, through which the oil is conveyed to the wick. *a* is an aperture for filling *b* with oil, and closed by a metallic screw-plug. The wick is a circular argand burner with double currents of air and with glass chimney, *c*. The metallic bearer or gallery, *f*, of the chimney can be made, as in moderateur oil lamps, to slide upwards and downwards for the purpose of adjusting the height of the bent narrowed portion of the glass so as to produce the best flame. This narrowed part of the glass should stand about three-eighths of an inch above the wick, as indicated by the dotted lines *d* and *e*, so that the greater part of the flame, which should be about 6 to 8 centims. high, is above the narrowed portion of the glass. If the glass is too high the flame either smokes or is ruddy, and when too low the flame is small and hardly emits any light. The oil reservoir of this lamp does not become heated, since it is kept cool by the strong current of air drawn in by the combustion. In one of the recently published numbers of the "Journal of the Society of Arts," the petroleum lamps of Silber are very highly commended. These lamps yield a light equal to that of twelve to forty wax-candles, while the construction is such that they can be used with either mineral or fatty oils alternately, and without the necessity of trimming the wicks. We have already alluded to the so-called benzoline or sponge lamps (see p. 639).

III. *Gas.*

General Introduction and Historical Notes.

For many hundreds of years it has been known that fossil coals yield a combustible gas, and even in very ancient times the observation has been made that large quantities of combustible gases were sometimes evolved from coal and other mineral seams, also from salt-mines, &c. The soil contains in many localities such a quantity of gas that by boring a hole the escaping gas may be employed for the purposes of illumination. In the neighbourhood of Fredonia, State of New York, a native permanent source of gas exists, which having been accidentally discovered by the pulling down of a mill situated on the banks of the river Canadaway, has been, by boring into the bituminous limestone, enlarged, and a gasholder constructed. The native gas now serves for the purpose of illuminating the locality. The quantity of gas collected in twelve hours amounts to about 800 cubic feet, and consists, according to Fouqué's researches, of a mixture of marsh-gas (CH_4) and hydride of ethyl (C_2H_6). In the Szlatina salt-mine, situated in the Marmaro Comitate (Hungary), illuminating gas is constantly evolved at a depth of 90 metres below bank from a marly clay which is interspersed between the layers of rock-salt. This phenomenon was known in 1770, and the gas is now collected in a gas-holder and used for lighting up the mine. A small quantity of gas is also evolved in the Stassfurt rock-salt mines. The Rev. Mr. Imbert, who as a missionary has travelled through China, states that in the Province of Szu Tchhouan, where many bore-holes for rock-salt have been made to a depth of about 1500 to 1600 feet, gas is permanently emitted and conveyed in bamboo tubes to places where it is used for lighting as well as heating purposes, more especially the heating of salt-pans in which the brine is evaporated. In Central Asia and near the Caspian Sea there are at several localities so-called eternal fires, which are due to the constant evolution of gas from the soil. Similar phenomena are observed at Arbela in Central Asia, at Chitta-Gong in Bengal, and elsewhere, while now and then large volumes of gas emitted in the coal-pits and conveyed to bank by means of iron pipes are suffered to burn for several days.

As regards the artificial production of gas from coals, Clayton and Hales, 1727 to 1739, made the first observations on this subject; while the Bishop of Llandaff, 1767, exhibited how the gas evolved from coal might be conveyed in tubes. Dr. Pickel, Professor of Chemistry at Würzburg, lighted his laboratory, 1786, with the gas obtained by the dry distillation of bones. At about the same period Earl Dundonald made experiments on gas-lighting at Culross Abbey; but it should be observed as regards these experiments that they were made more with the view to obtain tar, and the gas evolved by the distillation of the coals was considered a curiosity. The real inventor of practical gas-lighting is William Murdoch, who in 1792 lit his workshops at Redruth, Cornwall, with gas obtained from coals. His operations remained unknown abroad for some ten years, and hence the French consider Lebon as the inventor of gas-lighting, since he lit (1801) his house and garden with gas obtained from wood. The first more extensive gas-work was established in 1802 by Murdoch, at the Soho Foundry, near Birmingham, the property of the celebrated Boulton and Watt: and in 1804 a spinning-mill at

Manchester was lighted with gas. From that period gas-lighting became more and more generally adopted in factories and workshops, but not before the year 1812 did this mode of lighting become introduced into dwelling-houses and streets, a few of which in London were lit with gas in this year; while in Paris gas was first introduced in 1820. From that year gas-lighting may be said to have become of general importance in Europe, and now there is hardly any important place on the Continent where it is not in use, while as regards the United Kingdom in no portion is gas-making and lighting so general over town and country as in Scotland. Among the more recent improvements in this direction are Pettenkofer's wood and peat gas manufacture, and Hirzel's gas from petroleum residues. The principle of gas-lighting is, as has been already stated, the same as that of candles and oil lamps, but the raw materials in use for gas-making are not by themselves suited for illumination, and it is therein that the great improvement is to be found.

Raw Materials of Gas-Lighting. These are coals, wood, resin, fatty substances, oil, petroleum, and water, and according to the material employed the gas obtained is designated as coal wood, resin, oil, petroleum, and water gas.

Coal Gas.[*] I. Coals consist of carbon, hydrogen, oxygen, and small quantities of nitrogen, mineral matter, or ash, and contain, further, a larger or smaller quantity of iron pyrites. Technically we distinguish in England gas coals, steam coals, and household coals. As regards the first—the so-called cannel coals usually excepted—they belong to the class termed caking coal, for the reason that this kind of coal when submitted to heat softens and becomes agglutinated. According to H. Fleck, the best kinds of gas-coals contain upon 100 parts of carbon 2 parts of fixed (*gebundenen*) and 4 parts of disposable (*disponiblen*) hydrogen. Among the best gas-coals are the so-called cannel coals, the term cannel being a corruption of candle, as in former times pieces of these coals were in some parts of Scotland and Lancashire used by the poorer people to burn instead of candles. Cannel coal is chiefly found in Scotland and Lancashire, although there exist seams of cannel coal in some of the pits of Durham and Northumberland. The Boghead coal, or Torbane Hill mineral, is not properly speaking a cannel coal, and will—excepting as specimens in museums—soon have disappeared altogether; for gas manufacture it has already become quite obsolete. In France and Belgium—in addition to large quantities of imported English gas-coals and Scotch cannel—the coals of Mons and Commentry are used, while in Germany the Saxony, Silesian, Westphalian, and Rhenish coal-pits yield excellent gas-coals. Gas-coal should be as much as possible free from sulphur, and should further contain only a small quantity of ash; but in practice these points are less attended to, because the defects of one kind of coal are by good gas-makers counterbalanced by the better properties of other kinds.

1 cwt. (=50 kilos.) of German coals yields on an average 14 cubic metres, or 500 English cubic feet of gas, and 35 kilos. or 150 parts by bulk of coke. In England it is usual to compute the quantity of gas yielded per ton of coals: on an

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[*] 1 cubic metre = 35·31 English cubic feet.
40·22 Bavarian ,, ,,
32·34 Rhenish ,, ,,
31·65 Vienna ,, ,,
1000 cubic feet English = 28·31 cubic metres.
1138 Bavarian cubic feet.
915 Rhenish ,, ,,
896 Vienna ,, ,,

average the Newcastle coals yield about 9000 to 9500 cubic feet of gas per ton of coals; cannel coals vary in yield from 10,000 to 12,000; as regards the Boghead variety it gave about 15,000 cubic feet of gas, but much depends upon the mode of distillation and the length of time this operation is continued. It should be borne in mind that the best illuminating gas is given off during the first hours of the distillatory process; the latter products, though adding greatly to the bulk of the mixture, contain much of the comparatively useless gases and diluents. The mode of decomposition of the gas-coals may be elucidated by the following diagram, 100 parts of coal consisting of:—

Carbon	78·0	yield	Coke	70—75
Hydrogen	4·0		Illuminating gas	30—25
Nitrogen	1·5		Tar	
Sulphur	0·8		Ammoniacal water	
Chemically combined water	5·7			
Hygroscopic water	5·0			
Ash	5·0			
	100·0			100·0

Products of the Distillation. These may be classified into four chief products:—

I. Coke.	Carbon	90—95
	Sulphuret of iron (Fe_7S_8)	10— 5
	Ash	
		100

II. Ammoniacal liquor.	Main constituents.	Carbonate of ammonia,	$2(NH_4)_2CO_3+CO_2$
		Sulphide of ammonium,	$(NH_4)_2S$
		Chloride of ammonium,	NH_4Cl
		Cyanide of ammonium,	NH_4CN
		Sulphocyanide of ammonium,	NH_4CNS

III. Tar.	Hydro-carbons.	Fluid.	Benzol,	C_6H_6	
			Toluol,	C_7H_8	
			Xylol,	C_8H_{10}	
			Cumol,	C_9H_{12}	
			Cymol,	$C_{10}H_{14}$	
			Propyl,	C_3H_7	
			Butyl,	C_4H_9, &c.	
		Solid.	Naphthaline,	$C_{10}H_8$	
			Acetylnaphthaline,	$C_{12}H_{10}$	
			Fluoren,	(?)	
			Anthracen,	$C_{14}H_{10}$*	
			Methylanthracen,	$C_{15}H_{12}$	
			Reten,	$C_{16}H_{12}$	
			Chrysen,	$C_{18}H_{12}$	
			Pyren,	$C_{16}H_{10}$	
	Acids.		Carbolic,	C_6H_6O	
			Cresylic (cresol),	C_7H_8O	
			Phlorylic (phlorol),	$C_8H_{10}O$	
			Rosolic,	$C_{20}H_{16}O_3$	
			Oxyphenic,	$C_6H_6O_2$	
			Creosote, consisting of three homologous substances,	$C_7H_8O_2$	Combinations of oxyphenic acid and acids of methyl homologous therewith.
				$C_8H_{10}O_2$	
				$C_9H_{12}O_2$	

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* Has become important as a source of alizarine, in consequence of the discovery of Graebe and Liebermann, 1869.

III. Tar.	Bases.	Pyridine,	C_8H_5N	Leucoline,	C_9H_7N	Coridine,	$C_{10}H_{15}N$
		Aniline,	C_6H_7N	Iridoline,	$C_{10}H_9N$	Rubidine,	$C_{11}H_{17}N$
		Picoline,	C_6H_8N	Cryptidine,	$C_{11}H_{11}N$	Viridine,	$C_{12}H_{19}N$
		Lutidine,	C_7H_9N	Acridine,	$C_{12}H_9N$		
		Collidine,	$C_8H_{11}N$				
	Asphalte forming compounds	Anthracen					
		Empyreumatic resins					
		Carbon.					

IV. Illuminating gas.	α. Illuminating or light-yielding constituents.	Gases.	Acetylen,	C_2H_2	
			Elayl,	C_2H_4	
			Trityl,	C_3H_6	
			Ditetryl,	C_4H_8	
		Vapours.	Benzol,	C_6H_6	
			Styrolen,	C_8H_8	
			Naphthaline,	$C_{10}H_8$	
			Acetylnaphthaline,	$C_{12}H_{10}$	
			Fluoren,	(?)	
			Propyl,	C_3H_7	
			Butyl,	C_4H_9	
	β. Diluents, or light-bearers.		Hydrogen,		H_2
			Methylhydrogen,		CH_4
	γ. Impurities.		Carbonic oxide,		CO
			Carbonic acid,		CO_2
			Ammonia,		NH_3
			Cyanogen,		CN
			Sulphocyanogen		CNS
			Sulphuretted hydrogen,		SH_2
			Sulphide of carbon,		S_2C
			Sulphuretted hydrocarbons		
			Nitrogen,		N

Manufacture of Coal Gas. Whether coals, resin, wood, peat, or other materials are employed, the manufacture of gas involves the three following chief operations, viz.:—*a*. The obtaining of crude gas by the process of distillation. *b*. The separation of tarry and other condensable matters. *c*. The purifying of the crude gas so as to render it fit for use.

a. The distillatory process or making of crude gas is effected by the application of a high temperature—above red-heat—and exclusion of air, and is carried on in vessels which are technically termed gas retorts or simply retorts.

Retorts. The retorts were in the earlier days of gas-lighting always made of cast-iron and of cylindrical shape, but for the last twenty years fire-clay retorts have become very generally used, though they have not altogether superseded the use of cast-iron retorts, which were found inconvenient for only two reasons, viz., for wearing out too rapidly, and for not admitting of being raised to the very high orange-heat, which has been adopted for the distillation of some kinds of cannel coals. As regards the size of the retorts, this varies according to the requirements of the works, but generally the retorts are sufficiently large to hold 100 kilos. of coal, leaving from 0·5 to 0·6 of the interior space unfilled for the purpose of affording room for the expansion of the coals. The diameter of such a retort is about 54 centimetres in the larger axis, and 43 to 45 centimetres in the smaller axis, by a length of 2·5 to 3 metres. One end of the retort is usually closed, although in some large gas-works, as at Edinburgh, Glasgow, Paisley, fire-clay retorts of very great length and open at both ends are in use, being fired by two furnaces situated at each end. In some of the London gas-works, retorts are in use not made of fire-clay, in one or more pieces, but built up with fire-bricks or slabs of fire-clay, of a peculiar shape, and made for the purpose in Wales; these slabs are put together with a cement of pure quartz sand and about 1 per cent of lime, or a clay which becomes pasty and adhesive in very great heat. Retorts of this kind are cheaper and stand five years' wear. Retorts made of heavy boiler-plate rivetted together, as well as forged iron retorts, welded together like the iron mercury bottles, are also in use, but of course are, in the furnaces, protected from the direct action of the fire by properly built arches and coverings of fire-bricks.

Mouth-piece and Lid of Retorts. The retorts are always fitted with a separate mouth-piece, to which during the process of distillation the lid is fastened; this mouth-piece is always made of cast-iron, even in the fire-clay retorts, to which it is fitted by a flange on the retort, the flange of fire-clay being provided with six to eight holes for putting in the screw bolts for the purpose of making a good joint. In order to get a gas-tight joint a mixture of iron filings and gypsum is used, which is made into a paste with an aqueous solution of sal-ammoniac. The mouth-piece is fitted with a short tube for the purpose of giving vent to the gases and vapours evolved during the distillation As the mouth-piece is placed outside the furnace, it is generally of longer duration than the retorts, and these are moulded to suit the mouth-piece.

Fig. 282.

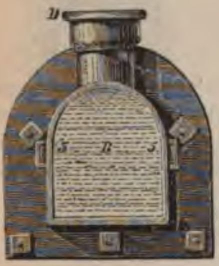


Fig. 283.

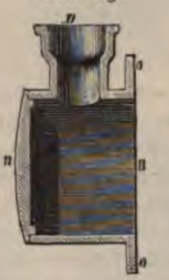


Fig. 284.

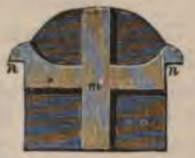


Fig. 285.

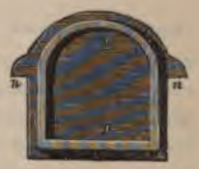


Fig. 282 exhibits the front view of a mouth-piece of a ∩-shaped retort. Fig. 283 exhibits a section. B is the opening at the retort end; *n* is the lid for closing the retort during the distillation. At *ss*, Fig. 282, are seen the cast-iron eyes intended to support the malleable iron bars for the support of the lid. *oo*, Fig. 283, is the flange wherewith the mouth-piece is fitted to the retort. D is the short piece of tube. Fig. 284 is a front view of the cast-iron lid of the retort; and Fig. 285, a view of the side of the lid turned towards the retort. As will be observed, the lid fits accurately into the opening of the retort. The method of closing or rather tightly fastening the lids of gas retorts is exhibited in Fig. 286, being a side view of the mouth-piece. *mm* are the malleable iron bars on which the lid is supported by means of the projections, *nn*, Fig. 284. Through the bars *mm* are cut openings, through which the cross-bar *p* is put, and in its centre a hole with screw thread, into which is made to fit a screw-bar and handle, *a*. By turning the screw, the lid is forced tightly against the rim of the mouth-piece; but in order to secure a gas-tight joint, a lute is used consisting of some clay or spent purifier lime and clay mixed.

Another mode of fastening the lid is exhibited in Fig. 287, being also a side view. The bars *mm* are in this instance bent at one end where the cross-bar *a* is to be placed. To that cross-bar is fitted at right angles another bar, H, provided at one end with a heavy iron ball, and at the other with a knee-bend, so that by pulling the ball downwards the lid, *n*, is tightly fastened.

Retort Furnaces. The retorts are placed in a furnace in the manner exhibited in Fig. 288, that is to say they are placed horizontally and supported by brickwork—technically benches. The mouth-piece projects from the furnace, each of which may contain two to three, five to seven, or even twelve to sixteen retorts, as in large gas-works, in which case the lower rows are of fire-clay, the higher of iron.

FIG. 286.

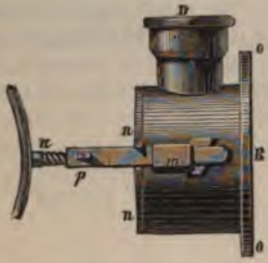
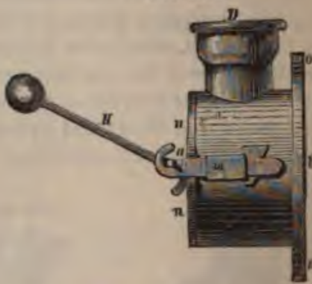


FIG. 287.



Charging the Retorts, and Distillation. The retorts are in some works charged by means of a large scoop, which being filled with the quantity of coals the retort is intended to be charged with, is carried by four men and then lifted into the retort, and being overturned fills the retort, after which the scoop is withdrawn and the lid of the retort fastened on. But in many gas-works the coals are thrown into the retorts with shovels. As soon as the retorts, which previously to being filled are always heated to red-heat or higher, are charged, and the lids closed, the evolution of gas is very strong, and continues so for some time, until after some four to five hours the distillation is finished, or at least the gas then given off is not worth collecting. In Scotland the distillation is not continued so long, three or three and a half hours being deemed. with good firing, quite sufficient, cannel coals giving off their gas more freely than caking coals. The lids are now loosened and the gas at the mouth of the retorts kindled in order to prevent explosion by its becoming, as would be the case if the lids were at once removed, mixed with air. The red-hot coke left in the retort is raked out and at once used for firing the furnaces, or put into iron wheelbarrows and wheeled out of the retort-house into the yard, there to be quenched with water and kept for sale. Cannel coals do not as a rule yield a good coke, but only broken-up black shaly breeze, which, however, along with some dead oil, is used in the Scotch gas-works for heating the retorts. On an average one-third of the coke obtained is required for firing the retorts.

The Hydraulic Main. We understand by the hydraulic main a vessel with which are connected the ascending tubes leading from the retorts. As a rule the hydraulic main is placed on the top of the furnace in which the retorts are ignited. The diameter of the ascending tubes varies of course with the size of the retorts, but is on an average 12 to 18 centimetres. The hydraulic main, of which B, Fig. 288, is a section at right angles to the longitudinal axis, is a wide pipe of cast-iron or of boiler-plates rivetted together, and having an average diameter of 30 to 60 centims. It is either cylindrical or ◠-shaped, and extends over the entire length of the row of furnaces. The hydraulic main is intended to act as a receiver for all the

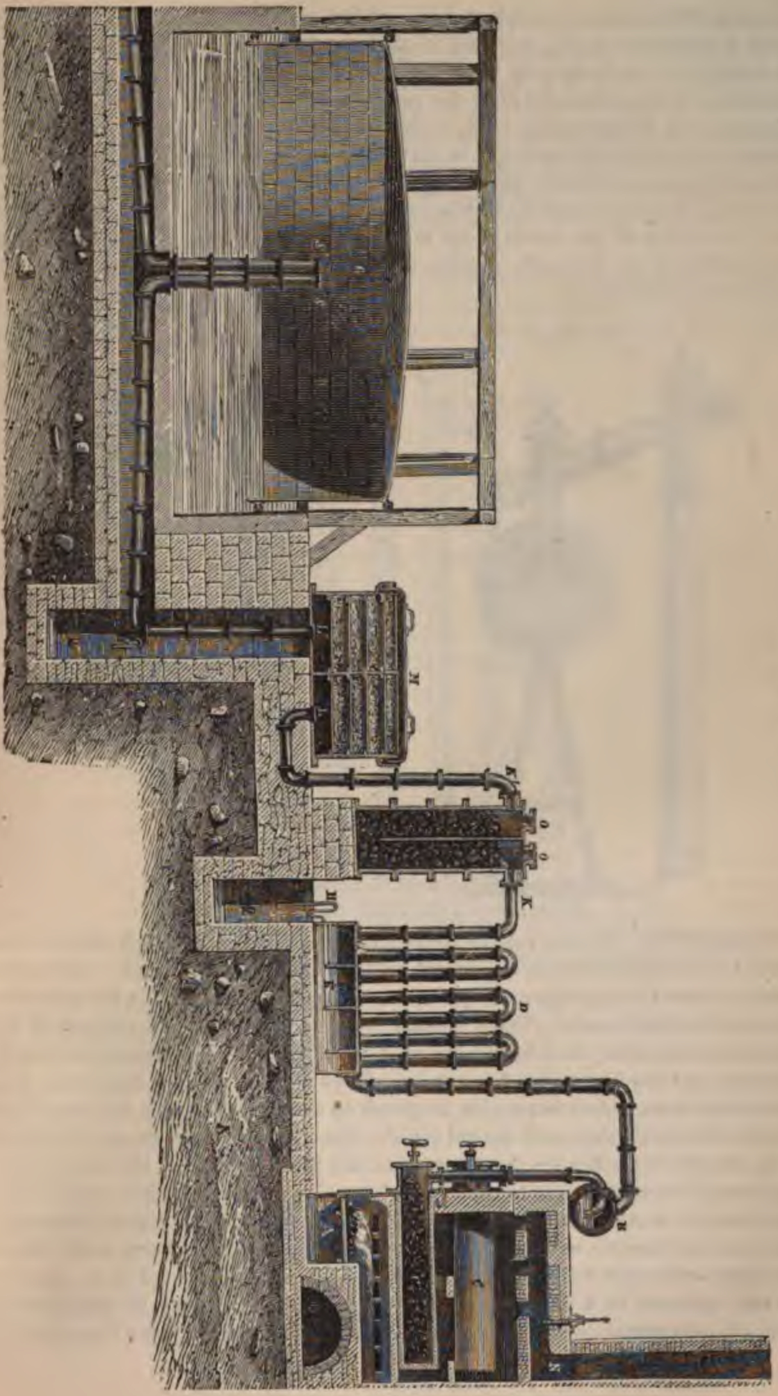


FIG. 288.

volatile products of the distillation, while at the same time it affords to every single retort a hydraulic valve, shutting it off from the other retorts, and preventing effectually any gas finding its way back to the retorts when opened at the mouth. The mode of connection between the retorts and the hydraulic main is shown in Fig. 289. A is the ascending tube; B the saddle-pipe; C the dip-tube carried downwards into the hydraulic main; D is the main; and *m* the liquid—viz. tar, or at the first starting of a gas-work, water. Fig. 290 exhibits a somewhat different mode of connecting the retorts and hydraulic main. There is fitted to this main a syphon tube for running off the excess of tar to the tar cistern, and on the top of the main is, as exhibited in Fig. 288, a wide iron tube for carrying off the gas to the condensing apparatus.

Fig. 289.

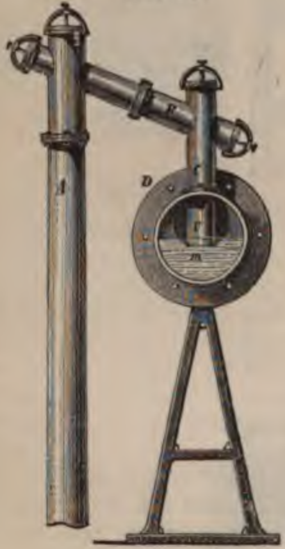
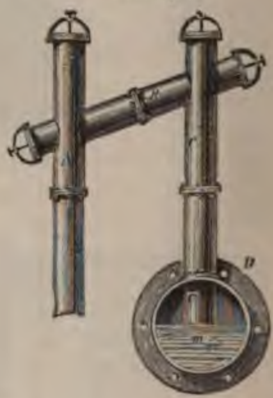


Fig. 290.

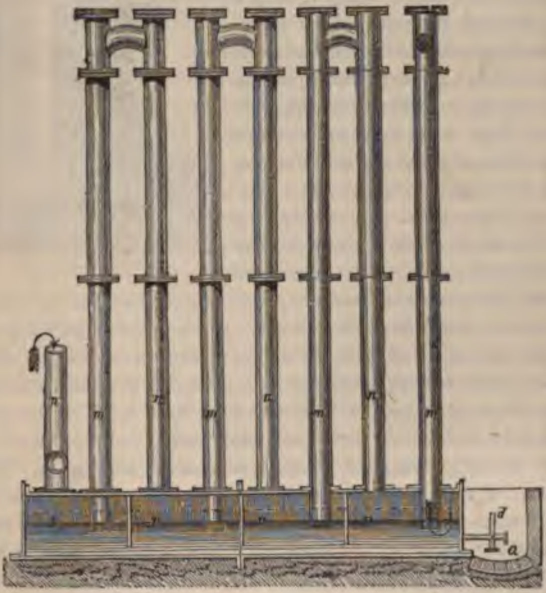


Cooling or Condensing Apparatus.

b. The volatile products of the distillation which are not condensed in the hydraulic main are carried off with the permanent gases. The reader should observe that a comparatively very high temperature prevails in the ascending tubes and hydraulic main. These volatile products are gas, steam vapours of tar, the steam containing in solution and suspension various ammoniacal compounds. Before the gas can be purified it has to be cooled and deprived of a number of substances which are in fact impurities, inasmuch as they would impede the flow of gas through the pipes if they were not got rid of. The condensing process may be carried on in various ways, but on the large scale the most efficient is the very simple expedient of causing the gas to pass through a series of cast-iron pipes, as exhibited in Fig. 291, in vertical section; also in D, Fig. 288. These tubes, placed in the open air—in warm climates or in hot summer weather arrangements being made to cool the pipes externally by a stream of water—are connected with each other at the top, and rest in a large cast-iron tank, *p*, which by means of partitions is divided into compartments not communicating with each other, being hydraulically locked. Each compartment is fitted with an inlet, *m*, and an outlet, *n*. In this tank the gas-water or ammoniacal liquor and tar are collected, while the height these fluids should occupy in the tank is regulated by a tube, *d*, or as seen in Fig. 288, at H, by a syphon tube. The condensed liquids flow to the brickwork tank, Q, and thence to the tar cistern. The inlet tubes dip to some depth into the fluid so as to force the gas to pass through it. The size, number, and height of these condensing tubes depends on the quantity of gas which has to be cooled in a given time; on an average 50 to 90 square feet of surface of tubes is allowed for 1000 cubic feet of gas to be cooled per hour.

The Scrubber. In many of the larger gas-works the gas, after it has issued from the tube condenser, is passed through an apparatus termed the scrubber, for the purpose of more completely depriving it of tarry matter before sending it on to the purifiers,

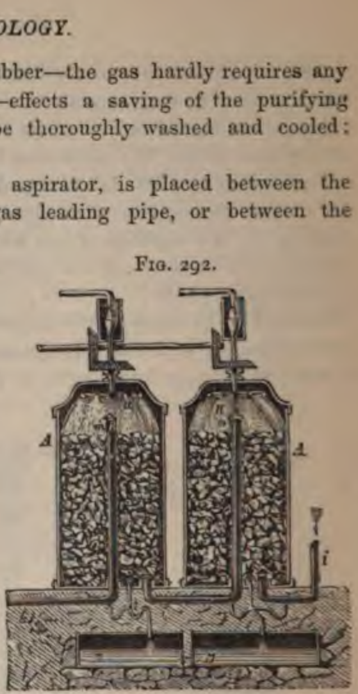
FIG 291.



and also for getting rid of the ammonia and sulphur compounds. The *rationale* of the mode of action of the scrubber is similar to that often employed on a minute scale in practical chemistry, when a gas or vapour is passed through a glass tube filled with pumice-stone, so that in a limited space a great surface is provided. The scrubber consists of cylindrical cast or malleable iron chambers of sufficient size, and filled with lumps of coke or fire-brick, which are constantly moistened with water. Fig. 292 exhibits a sectional view of a scrubber, also seen in Fig. 288 at *o o*. The cylinder has a diameter of 1½ to 1¼ metres, by a height of 3 to 4 metres; the vessel is filled with coke, which is kept moist by means of water introduced by the rotating perforated tube, H. The inlet of the gas is at *i*; it proceeds upwards through the column of coke and on reaching the top passes off downwards through *m* to the second scrubber. At the lowest bend of the exit or outlet tubes a syphon pipe is fitted for the purpose of draining off water and tarry matters which collect in the reservoir, M. The use of the scrubber—the gas hardly requires any additional pressure to be carried through it—effects a saving of the purifying materials, lime, &c., by causing the gas to be thoroughly washed and cooled: in other terms—mechanically purified.

Exhauster. This apparatus, also termed the aspirator, is placed between the hydraulic main, being connected with the gas leading pipe, or between the condensers and the purifiers. It is intended to suck or pump the gas from the retorts so as to diminish their internal pressure. This pressure amounts in some cases to nearly 15 lbs. to the square inch, and it was found that under that pressure a great deal of gas was lost through the pores of the fire-clay retorts, especially when new, being then not coated with a film of graphite which afterwards acts as an impermeable layer. The aspirators also serve to remove the gaseous mixture as rapidly as possible from the red-hot retorts and coke, and thus prevent the partial decomposition of valuable illuminating constituents of the gas, by which decomposition, moreover, the retorts, iron as well as fire-clay, become lined with a graphite-like coke, which impairs the conducting power for heat, as well as decreases the internal cubic capacity of the retorts. The introduction of exhausters dates from 1839, when Grafton made and tried the first. His arrangement was—a box filled with water for about three-fourths of its capacity, while in the box, on an axis projecting outside, through gas- and water-tight stuffing boxes, four circularly-bent scoops were fixed, so that on a rotating motion being imparted to the axis, and thereby to the scoops, a partial vacuum was formed, and the gas inspired into the apparatus, and thence carried off by side tubes. This apparatus has never been of any practical use in gas-works. Next, the so-called bell exhauster was used; the principle of this apparatus—similar in construction to that in use in paper mills—being in reality nothing else than a hydraulic air-pump, consisting of two or three large bell-shaped iron vessels, connected together and placed in tanks filled with water, and moved slowly upwards and downwards by mechanical power. Under each of these bell-shaped vessels an inlet and outlet pipe is fitted provided with valves. There have been a great many variously constructed exhausters proposed; some of these, Anderson's for instance, are similar to the cylinder blowing machines in use with blast furnaces; others again are similar in construction to the double-acting air-pumps of low-pressure marine steam-engines; some to centrifugal pumps. With the fire-clay retorts, now very generally adopted in gas-works, the use of exhausters is almost a necessity, and the apparatus is always fitted up with new gas-works. Of course an accessory of the exhauster is a small steam-engine and boiler.

FIG. 292.



Purifying Gas. *c.* The crude gas having been passed through the apparatus just described, and mechanically purified, is sent on, as it is technically termed, to the purifiers, in order to eliminate by chemical means such substances as sulphuretted hydrogen, carbonic acid, and various ammoniacal compounds, carbonate of ammonia, sulphuret of ammonium, cyanide of ammonium, &c.; and also some of the compound ammonias, as, for instance, aniline, iridoline, &c. At the outset of the gas-lighting industry, quick-lime was the only material employed for purifying purposes, this substance being at first employed in the form of a thick milk of lime, the purifier being so constructed that the crude gas was brought into intimate contact with the fluid, which, in order to prevent the lime from forming a sediment, was kept in constant motion by a stirring apparatus; while the purifier, made of cast-iron, was provided with inlet and outlet pipes for the gas, a pressure gauge, and the necessary syphon pipes and valves for letting out the waste milk of lime and re-filling the vessel. Variously arranged wet lime purifiers have been devised, and among them some which act also as exhausters; but notwithstanding the very satisfactory results obtained by the use of wet lime purifiers, the gas being very effectually freed from carbonic acid, sulphuretted hydrogen, and ammonia, there is the defect—first, of the back pressure on the retorts and other apparatus; and secondly, a difficulty in the mode of so disposing of the very fœtid waste lime liquor as not to create a nuisance; hence it is that the wet lime purifiers have been almost entirely superseded by the so-called dry lime purifiers. These are large square iron boxes fitted inside with movable trays resting on ledges and provided with sieve-like perforations, and either made of iron gratings or iron plates, or even wooden boards, on which the previously slaked and somewhat moist lime is carefully placed in layers of uniform thickness to a height of 20 centimetres, there being in every purifier box from five to eight frames. The purifier is usually divided into two compartments by a partition, so that the gas which enters from the bottom of one compartment has to ascend through the layers of lime of the inlet compartment, and to descend through those of the outlet compartment. The gas passes through the layers of dry lime readily enough and almost without producing any back pressure, and there is no necessity to render the lime more porous by the addition to it of either moss, sawdust, chopped straw, &c. As to the quantity of lime required for the purpose of purifying a certain volume of gas, it is stated that for 1000 cubic feet of crude gas from Newcastle coals, 2·6 kilos. of unslaked quick-lime are required. With careful selection of the gas-coals to be carbonised, and a well-conducted distillation and mechanical purification of the crude gas, the lime purifying process, especially if wet and dry purifiers both are used, as is the case in some of the largest gas-works in Scotland, yields excellent results, and there is no need for any other purifying materials; while the spent lime, as is the case in Scotland, is found useful as a manure, as well as for building purposes with some fresh lime and sand. It is, however, true that in many places the gas thus made is too impure for use in dwelling houses, and a more complete elimination of the ammonia and some of the sulphur compounds is found to be absolutely necessary. Since 1840 an immense number of gas-purifying materials and contrivances have been brought forward and tried but again abandoned. It is entirely beyond the scope of this work to enter into more than a very slight sketch of the various gas purifying processes; but we give the following particulars on this subject.

It cannot create any surprise when we find that acids and metallic salts should have been called in to aid the absorbing of the ammonia and sulphuretted hydrogen from coal-gas. Protosulphate of iron has been here and there resorted to, of course in aqueous solution. Mallet (1840) commenced the use of the residue of the chlorine manufacture, crude chloride of manganese, for the same purpose. Far more important is the method first suggested in 1847 by R. Laming, and now generally known as the Laming purifying process. As originally patented, the mixture was composed of protochloride of iron with quick-lime or chalk, and in order to keep the mass porous sawdust was added. Instead of protochloride of iron, sulphate of iron is now more generally used, and mixed with previously sifted and slaked lime, and one-fifth to one-fourth of its bulk of sawdust. The mass is then placed in beds or layers exposed to open air, moistened with water, and is, after twenty-four hours, fit for use in the same apparatus as is employed in the dry lime purifying process. According to the results of the scientific researches of A. Wagner (1867), Gélis (1862), of Brescius, Deicke, and others, the peroxide of iron of the Laming mixture becomes converted by the sulphuretted hydrogen into sesquisulphuret of iron (Fe_2S_3), and by exposure to air—revivifying process, for which purpose old purifiers are used, air being forced through—the sulphur is separated again, and oxide of iron mechanically mixed with sulphur is left. This mixture may be used several times, and as mentioned in the earlier pages of this work, the sulphur may be advantageously extracted from this mixture. Gauthier-Bouchard, at Paris, has proved that the spent Laming mixture may be used on the large scale for manufacturing Berlin blue and yellow prussiate of potash; while Menier, at Marseilles, prepares annually 12 to 15 tons of sulphocyanide of ammonium from the spent gas-purifying materials. Very recently (1869) the proposition has been made to withdraw the benzol contained in illuminating gas by passing the gas through heavy oils of tar, from which the benzol, to be used for aniline making, is to be separated by fractioned distillation, and the gas again rendered luminous by passing it through benzoline, light petroleum spirit. It is evident that considering the great bulk of gas to be operated upon, this proposal or suggestion will be difficult to carry out in practice, and also costly in consequence of the apparatus required.

Gas-holders. These apparatus, sometimes but less correctly termed gasometers, serve as well for the purpose of storage of the great bulk of the gas as for causing a sufficient pressure, so as to regulate its flow through the street mains and burners. The gas-holder consists of three parts, viz.:—1. The tank, a cylindrical water-tight, more or less deep vessel, with vertical sides, filled with water as a hydraulic lute. 2. The bell, or rather inverted cylinder, which can move freely between the stand-pillars by the aid of grooved rollers or pulleys, which work on iron bars fitted against the stand-pillars. 3. The large inlet-pipe which communicates with the purifiers, and the outlet-pipe which communicates with the street mains, each being supplied with valves and syphon-boxes for the purpose of collecting any water which might condense or otherwise find its way into these pipes.

The tank was in former days made of wood, then, when the size of the gas-holders was increased, of cast-iron plates fitted with flanges provided with holes for screw-bolts, the joints being filled with cement so as to make a water-tight vessel. Now the tanks are constructed by digging to a greater or less depth into the soil, the bottom and sides being laid in brickwork with a water-tight cement backed by a puddling of clay. In some few cases the tank is constructed as exhibited in Fig. 293, where a cone remains covered by brickwork, but as water is generally plentiful, and is less costly than the expense attending this arrangement, it is not usual. The bell or holder is always made of sheet-iron plates rivetted together, care being taken either to put red-lead putty, or brown paper soaked with red-lead paint or thick boiled tar between the overlappings of the plates so as to obtain good joints. The plates are inside and outside painted with iron-paint or coated with boiled coal-tar. Formerly, with gas-holders of a capacity varying from 30,000 to 80,000 cubic feet, the bell was suspended by means of iron chains led over pulleys fastened to the stand-columns and provided with heavy weights for the purpose of counterbalancing the too great weight of the iron-holder and to regulate the pressure exerted upon the gas; but with the very large holders now in use, and the practice of building them of thinner iron plates, the holders are simply made to move freely between the stand-columns as exhibited in Fig. 293. In order to gain space with the same depth of tank, the so-called telescopic gas-holders are constructed, being, in fact, one or more cylinders fitting into each other and capable of sliding upwards and downwards, the topmost cylinder only being fitted with a roof, while a gas-tight joint is obtained by a hydraulic lute. The inlet and outlet mains are of cast-iron, and open just a few inches above the level of the water in the tank (Figs. 288 and 293). A peculiar construction of gas-holder, invented by Pauwels, at Paris, and in use in some of the gas-works of that city, is exhibited in Fig. 294. The inlet and outlet pipes, *a* and *b*, are in this gas-holder connected with the roof, and consist of several pieces with joints fitted with gas-tight stuffing-boxes, the arrangement being readily understood from the engraving. The advantage is that all chance of flooding of the inlet and outlet pipes is prevented, but the arrangement is expensive and not compatible with telescopic gas-holders; moreover, the level of the water in the tanks of gas-holders

FIG. 293.

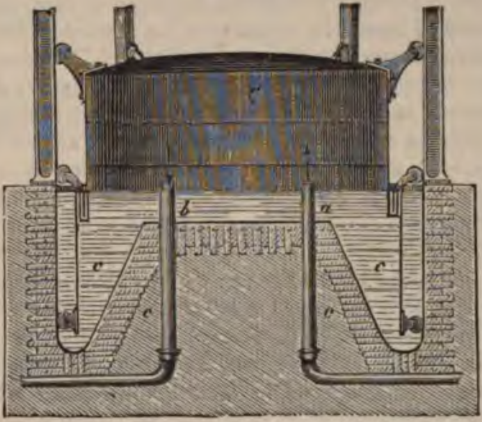
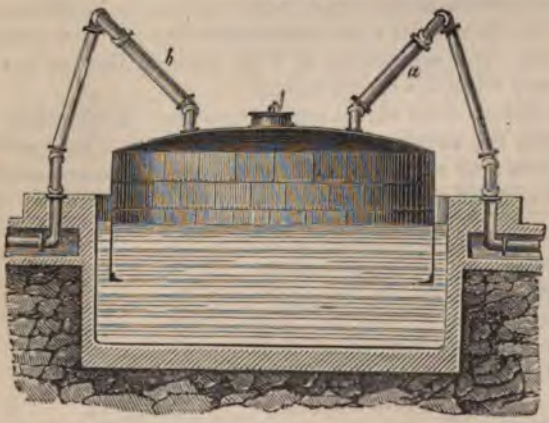


FIG. 294.



is rarely, if ever, subject to any great increase in height, because a drain-pipe is fitted to the upper rim of the tank for carrying off rain-water. Gas-engineers well enough know that it is difficult in many cases to prevent leakage from tanks so effectually that there should be much risk of the sudden flooding of the inlet and outlet pipes by a rush of water. Small gas-holders are often provided with a scale, the divisions of which correspond to certain quantities of cubic measure; but large gas-works are nearly all fitted with a station-meter, through which all the gas made has to pass previous to entering the gas-holders, and by means of this meter a control is kept over the quantity of gas made. The cubic capacity of every gas-holder is of course accurately known. The size of the gas-holders varies; some at very small works, for villages, railway-stations, country-seats, &c., are only 1000 to 3000 cubic feet capacity, while there exist gas-holders of enormous size, 45 metres diameter by 20 in height, which contain 1 million cubic feet. According to Riedinger's rule, the cubic capacity of a gas-holder should be equal to 2 to 2½ times the average daily quantity required.

The filling of a gas-holder is proceeded with in the following manner:—The outlet main-pipe having been shut off by the closing of the valve fitted to it, gas is admitted through the inlet-main into the holder; the gas accumulating in the latter exerts a pressure upon the water in the tank, which consequently is depressed inside the holder and rises higher outside it, while gradually the holder is lifted by the force of the gas, the inlet valve being shut off as soon as the holder is filled to within about 20 centimetres of its height. When the outlet valve is then opened the gas flows into the street mains, the pressure being obtained from the weight of the holder. In order to ascertain the quantity of the gas made, it is measured by a large gasometer, technically termed a station-meter, and placed between the purifiers and the inlet to the gas-holders. The construction of these station-meters is very similar to that of the ordinary wet gas-meters.

Very little is known as to the composition of the gas at the different stages of its manufacture from the moment it enters the hydraulic main to the moment it enters the street mains. The experiments of Firle, made at Breslau in 1860, are very valuable, but only relate to a special inquiry.

Firle tested coal-gas:—(*a*) after it left the condenser; (*b*) after it left the scrubber; (*c*) as taken from the washing-machine; (*d*) as taken from the purifier containing Laming's mixture; (*e*) as taken from the lime-purifier, consequently thoroughly purified gas as sent into the holder:—

	a.	*b.*	*c.*	*d.*	*e.*
Hydrogen	37·97	37·97	37·97	37·97	37·97
Marsh-gas	39·78	38·81	38·48	40·29	39·37
Carbonic oxide	7·21	7·15	7·11	3·93	3·97
Heavy carburetted hydrogens	4·19	4·66	4·46	4·66	4·29
Nitrogen	4·81	4·99	6·89	7·86	9·99
Oxygen	0·31	0·47	0·15	0·48	0·61
Carbonic acid	3·72	3·87	3·39	3·33	0·41
Sulphuretted hydrogen	1·06	1·47	0·56	0·36	—
Ammonia	0·95	0·54	—	—	—

Referring these figures to bulk, and taking 1000 cubic feet of crude gas as the unit quantity, we find the following proportions:—

	Cubic feet.				
	a.	*b.*	*c.*	*d.*	*e.*
Hydrogen	380	380	380	380	380
Marsh-gas	390	388	384	403	394
Carbonic oxide	72	71	71	39	30
Heavy carburetted hydrogens	42	46	45	46	43
Nitrogen	48	50	69	79	100
Oxygen	3	5	2	5	6
Carbonic acid	40	39	34	33	4
Sulphuretted hydrogen	15	15	5	3	—
Ammonia	10	5	—	—	—
	1000	999	990	988	966

The above results exhibit the changes which the composition of the gas undergoes during the purifying process as well as the action of the different apparatus. When 1000 cubic feet of gas composed as stated in (*a*) enter the purifying apparatus, in each of these there is taken up of the absorbable gases, chiefly carbonic acid, sulphuretted hydrogen, and ammonia, the under-mentioned quantities:—

For 1000 cubic feet in cubic foot measure:—

	Scrubber.	Washing-machine.	Laming's purifier.	Lime-purifier.
Carbonic acid	1	5	1	29
Sulphuretted hydrogen	—	10	2	3
Ammonia	5	5	—	—
Carbonic oxide	—	—	32	—
Oxygen	—	3	—	—

The original bulk of the gas decreases consequently steadily, and there remain of 1000 cubic feet of crude gas after leaving:—

The scrubber	994 cubic feet.
The washing-machine	971 ,, ,,
The Laming's purifier	936 ,, ,,
The lime-purifier	914 ,, ,,

This is correct, premising that the other constituents of the gas are unabsorbed, which really is so, as we may neglect the very small quantities of marsh-gas and heavy hydrocarbons, which are kept mechanically arrested in each purifying apparatus. The bulk of the gas is, however, slightly increased by an addition of atmospheric air. 1000 cubic feet of the crude gas (*a*) contain 51 cubic feet of oxygen and nitrogen; this quantity is increased:—

In the scrubber by	4 cubic feet.
In the washing-machine by	20 ,, ,,
In the Laming's purifier by	33 ,, ,,
In the lime-purifier by	55 ,, ,,

By this addition the total bulk of the gas in each apparatus is again increased, and amounts (taking account of the variable quantity of marsh-gas and heavy carburetted hydrogen compounds) for 1000 cubic feet unit quantity:—

After leaving the scrubber, to	999 cubic feet.
" " " washing-machine, to .	990 " "
" " " Laming's purifier, to .	988 " "
" " " lime-purifier, to... ...	966 " "

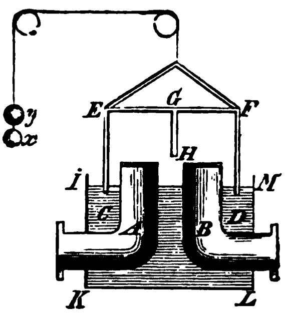
It is understood that temperature and pressure remain constant during the purifying process.

Distribution of Gas. Generally, in the United Kingdom, and as regards coal-gas also abroad, the gas is conveyed to the localities where it is to be burnt by means of cast-iron pipes laid underground. But so-called portable gas (*gas portatif*) is still made abroad and conveyed to the consumers in large gas-tight bags placed in cars, the bags being emptied at the houses of the consumers into small gas-holders. The materials from which this kind of gas is made are generally such (refuse of oil, oil of bones, very crude olive oil, resins, &c.) as yield a gas of far higher illuminating power bulk for bulk than coal-gas, so that a comparatively small bulk of gas will suffice for even a large number of burners. The pressure exerted upon the gas in the holders causes it to move through the pipes. The amount of this pressure is, however, usually regulated at the works by a peculiar mechanical contrivance, so as to make it as uniform as possible over the total length of the mains and service-pipes. Coal-gas being lighter than air has a tendency to rise, and for this reason it is considered preferable to build gas-works at the lowest level of the locality it is intended to supply, because a less pressure is sufficient for moving the gas through the mains. The pressure at the burners should be from 0·05 to 0·15 of an inch, water-gauge pressure, while at the gas-works a pressure of 2½ to 5 inches (water-gauge) is quite sufficient to force gas to any distance within a circuit of several miles.

The street mains are made of cast-iron, and laid under the pavement at a suitable depth, varying from 0·6 to 1·6 metre. The service-pipes in England and on the Continent are of malleable-iron or of lead, but in Scotland cast-iron pipes (even quarter and half-inch) are preferred and in general use. The large mains are put together by placing the spigot into the socket-end of each pipe alternately, and caulking in greased or tarred tow and pouring in molten lead. In Scotland the mains are now generally put on the lathe, and the spigot and socket ends turned true, so as to give a gas-tight joint simply by the aid of some red-led paint and putty and a collar of soft greased tow. Although carefully laid, the gas-mains give rise to more or less loss by leakage, which is stated to amount in some instances to 15 or 20, and even 25 per cent of the gas made and sent into the mains; but if street mains are cast vertically and the iron be of good quality, each pipe properly tested by hydraulic pressure for its soundness before being laid, and, moreover, first immersed in hot coal-tar and the joints well secured, leakage may be very much reduced, if not altogether prevented. The mains should have a sufficiently large bore for the quantity of gas to be conveyed through them, so as to reduce friction. They are not laid quite level even in level streets, but slope gently; while at the lowest level so-called syphon-pots are placed for the purpose of collecting any condensed water—the gas is almost saturated with water by being in contact with it in the gas-holders, although after some time a thin layer of empyreumatic matter covers the surface of the water, thereby preventing the gas becoming excessively saturated. These syphon-pots are fitted with a narrow iron tube reaching nearly to the surface of the pavement, being closed by a screw-cap, which, being unscrewed, a hand-pump may be screwed on, and any condensed water pumped out of the syphon-pot or box. For the purpose of connecting the burners with the service-pipes narrower tubes are used, made either of pure block-tin or of an alloy of lead and tin or of lead and copper; the latter are, however, not so readily bent, and have the disadvantage that there may be formed in them acetylen-copper, which, as proved by Crova, is a very explosive compound.

Hydraulic Valve. The valve represented in Fig. 295 is now almost superseded by valves of a totally different description, termed slide-valves, and worked similarly to those in use for the water-mains common in London streets. The valve represented in the engraving is placed near the gas-holders, and may serve either for shutting off the inlet-pipe to the holder or for the same purpose at the outlet-pipe. The valve consists of an iron vessel, I K L M, filled with water. The pipe A communicates with the gas-holder and B with the street main. The drum-like vessel, C E F D, is suspended over the pipes and is counterbalanced by the weights x and y. When the latter are removed the drum sinks, and the partition H, dipping in the water, cuts off the communication between A and B.

FIG. 295.



Pressure Regulator. This contrivance, acting automatically, is arranged for the purpose of regulating the supply of gas from the gas-holders to the mains. It consists essentially of a small gas-holder connected with a conical valve placed in the outlet-pipe, while the small gas-holder to which it is fastened is very accurately adjusted, or provided with counterweights, by means of which its position may be set at a certain supply either per hour or evening, as the case may be. If from some cause or other the consumption of gas increases the gas-holder will sink, and the opening in which the conical valve plays becomes larger, and consequently more gas passes through; if, on the other hand, the supply decreases, the consequence will be that too much gas enters the small holder from the large ones, and the former rising draws the conical valve with it upwards, thus more or less completely plugging the outlet-pipe.

Testing Illuminating Gas. The cause of the luminosity of the flame of gas is the ignited carbonaceous matter. Everything, therefore, which impairs the separation of the carbonaceous matter or chemically affects their proper ignition, decreases the luminosity of the flame; among these deteriorating causes are:—1. Excessive admission of air or of oxygen. A coal-gas flame burning in oxygen will be found to have lost its luminosity, and the same occurs, as is well known and exhibited in the Bunsen gas-burner, when gas is mixed with air previous to being ignited. 2. Carbonic acid. When red-hot or white-hot carbonaceous matter comes into contact with carbonic acid, there is formed carbonic oxide ($CO_2+C=2CO$), which burns with a blue, non-luminous flame. As elayl-gas (C_2H_4) becomes decomposed by red heat into methyl-hydrogen (marsh-gas, CH_4) and carbon (C), and as the latter reduces an equivalent quantity of carbonic acid to carbonic oxide, it is evident that the carbonic acid deprives half its bulk of elayl-gas of its illuminating power. Suppose an illuminating gas to contain 6 per cent of elayl-gas, and also 6 per cent of carbonic acid gas, the result will be the elimination of the luminosity of 3 per cent of elayl-gas. This proves the great importance of the complete removal of carbonic acid from gas by the lime-purifier.

Very little has been experimentally proved as to the relation existing between the illuminating power of a flame and the quantity of the separated carbonaceous particles; it is probable, however, that this relation is a direct one, and that therefore the luminosity of a flame is the stronger the larger the quantity of carbonaceous particles separated, provided, however, that the temperature of the flame be very high, because otherwise the flame will be either ruddy or smoky. Although by an increased access of air (as in the case of petroleum lamps provided with a glass chimney) the combustion may be increased so as to create a very high temperature of the flame and thereby a very white light, it is probable that this expedient (especially if applied to ordinary coal-gas) would cause a too sudden combustion of the carbon, rendering it useless for illuminating purposes. Supposing the illuminating power of a flame to be proportional to the quantity of carbonaceous particles separated, and applying this principle to some of the carburetted hydrogens occurring in purified illuminating gas, taking account more particularly of the gases (CH_2) so composed that by ignition they become decomposed into methyl-hydrogen and carbon, we have:—

Vol.		Vol.		Vols.	
1 elayl, C_2H_4,	which yields	1·0	of methyl-hydrogen and	2	of vapour of carbon.
1 trityl, C_5H_6,	,, ,,	1·5	,, ,, ,, ,,	3	,, ,, ,, ,,
1 ditetryl, C_4H_8,	,, ,,	1·0	,, ,, ,, ,,	4	,, ,, ,, ,,

and may assume the illuminating power of these three gases to be as 2:3:4. Taking the illuminating power of elayl-gas to be 100, the illuminating powers of the gases and vapours contained in purified coal-gas may be represented by the under-mentioned figures, the vapours having been calculated at a sp. gr. = 0°:—Elayl, 100; trityl, 150; ditetryl, 200; propyl, 250; butyl, 350; acetylen, 450; vapour of benzol, 450; vapour of naphthaline, 800.

The following figures exhibit the quantity of elayl-gas, for which can be substituted a combustible gas (hydrogen or marsh-gas) impregnated with the vapours of hydrocarbons at 0° and 15° for yielding an equal amount of light. Impregnation with—

		At 0°.	At 15°.
Vapour of propyl,	is equivalent to	11·500	25·700 vols. elayl.
,, ,, benzol,	,, ,, ,,	9·630	23·700 ,, ,,
,, ,, naphthaline,	,, ,, ,,	0·116	00·016 ,, ,,

When, therefore, 100 litres of hydrogen at 0° or at 15° are saturated with vapours of benzol, the illuminating power of the resulting mixture is equal to that which would ensue by mixing 100 litres of hydrogen with 9·6 or 23·5 litres of elayl-gas.

In order to saturate 100 English cubic feet of hydrogen- or marsh-gas with vapours of hydrocarbons, there are required of:—

	At 0°.	At 15°.
Vapours of propyl	500·00	1128·00 grammes
,, ,, butyl	17·00	58·00 ,,
,, ,, benzol	214·50	522·00 ,,
,, ,, naphthaline	0·32	0·32 ,,

For the purpose of carburetting hydrogen-gas with vapours of benzol to saturation, 2145 grms. of benzol at 0°, and 5220 grms. of the same at 15°, would be required for 1000 cubic feet of gas.

Methods of Testing Illuminating Gas. In order to ascertain the relative value of illuminating gas four different modes of testing are now in practical use, viz.:—1. Gasometrical test. 2. Specific gravity test. 3. Photometrical tests. 4. Erdmann's gas-testing apparatus.

1. The gasometrical test requires for its proper management an accurate knowledge of Bunsen's method of gas analysis.* Be it sufficient for our purpose here to

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Anleitzung zu einer technischen Leuchtgasanalyse giebt Adolf Richter; Dingler's polyt. Journal (1867), Bd. clxxxvi., p. 394.

mention that a mixture of anhydrous sulphuric acid and ordinary concentrated oil of vitriol has the property of absorbing the heavy hydrocarbons contained in illuminating gas, which absorption is best effected by bringing into an eudiometer containing the gas to be tested, a piece of coke moistened with the acid, and fixed on a piece of platinum wire. In order to ascertain the quantity of carbon of these compounds, the test, in which the decrease of bulk of the gas indicates the relative quantity of the hydrocarbons, is combined with two separate eudiometrical tests, the gas being first ignited by itself with an excess of oxygen, and the operation repeated with the gas after it has been acted upon by the sulphuric acid. The quantity of CO_2 obtained in the last instance is then deducted from that obtained by the first operation. Chlorine and bromine are very frequently employed to absorb the heavier hydrocarbons present in gas, these haloids combining with the hydrocarbons as a fluid residue. According to a method of gas analysis originally devised by O. L. Erdmann, and described by C. O. Grasse,* the gas first freed from any carbonic acid it may happen to contain is burnt from a burner connected with a small gas-holder, by the aid of oxygen; the water and carbonic acid formed are collected and weighed. 2. The estimation of the value of an illuminating gas by specific gravity is frequently employed in practice, as experience has proved that as a rule a higher illuminating power of gas (provided it be well purified and freed from carbonic acid), is intimately connected with its higher specific gravity; but it does not follow that a light gas is useless, while there ought to be taken into account the durability of the gas, by which is understood the length of time a cubic foot of the gas will burn under a certain pressure (as low as possible) from a given burner, and yield a certain light to be tested either by comparison with another kind of coal-gas or standard sperm candles by the photometer. In Scotland, the gas engineers when testing cannel and other coals always take into consideration and minutely estimate by means of very accurate apparatus these particulars, care being taken to manufacture the gas on the large as well as on the small scale, taking say ½ cwt. of coals, and to compare both. In most of the large Scotch gas-works, a separate experimental gas-work, with two or three retorts, and all the necessary apparatus, is to be met with, as it has been found that only by the use of judiciously selected mixtures of different cannel coals, a gas of high illuminating power, great purity, and average durability, can be supplied at the price now generally adopted per 1000 cubic feet.

Illuminating gas consists of a mixture of various gases and vapours, having different specific gravities, viz., elayl-gas, 0·976; methyl-hydrogen, 0·555; hydrogen, 0·069; carbonic oxide, 0·967; carbonic acid, 1·520. The specific gravity of the vapours present in coal-gas varies of course according to the bodies which are met with in the gas in the state of vapour; among these benzol is one of the most important for illuminating purposes. The estimation of the specific gravity of illuminating gas as a test of its quality is only of value if taken in connexion with other tests applied to the same gas. Dr. Schilling has constructed an apparatus for the purpose of taking the specific gravity of illuminating gas. This apparatus is based upon the fact that the specific gravities of two gases issuing from narrow apertures in a thin plate under equal pressure are to each other as the squares of their time of efflux. There are several more readily managed apparatus for estimating the specific gravity of illuminating gas, and among them those made by Mr. Wright, of Westminster. 3. Photometrical tests and apparatus, Bunsen's, Wight's. Desaga's

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* Journal für Prakt. Chemie (1867), cii., p. 257.

(Bothe's tangental photometer), and others are frequently employed for testing the value of gas and comparing its illuminating power with that of lamps or candles. As the kind of burner employed in these experiments has very great influence on the results, photometrical estimations of the value of gases require great care. 4. Erdmann's gas tester, introduced on the Continent in many gas-works since 1860, is a very useful and readily manageable instrument, based upon the fact that, as the value of an illuminating gas depends mainly upon the quantity of heavy hydrocarbons contained, that quantity may be measured by estimating the amoun of atmospheric air required to deprive the flame of the burning gas of a given size of all illuminating power.

Gas-meters. At first, in the early days of gas-lighting, the bargain between consumer and seller was to pay a certain sum per burner per hour, or to contract for a certain sum per annum for a given number of burners kept lighted from dusk till a certain hour of the night, at which time it was customary to have the turncocks of the gas-works at hand on their respective beats, to turn off the supply of the house, by shutting a tap placed on purpose in the service pipes; but although here and there in small towns in Italy France, Spain, and Germany, this arrangement still exists, it is the exception and not the rule; the latter being that the gas is sold by cubic measure as registered by instruments termed gas-meters, the construction of which is—especially in the United Kingdom—brought to such a high standard, that Mr. Rutter's remark is perfectly true—that gas is measured with greater accuracy than anything else either measured or weighed in commerce.

We distinguish between dry and wet meters; the construction of the former is briefly the following:—In a gas-tight metallic box are placed two or three bellows-like vessels which instead of being inflated by air, are inflated by the gas entering from the service pipe. When inflated to some extent an arrangement of springs and levers forces the gas out of the bellows again into the exit-pipe leading to the burners. The cubic capacity of the chambers (as the bellows-like arrangements are called) having been accurately adjusted, the movement of their walls is communicated to wheel-work, which being connected with dials, indicates in tens, hundreds, and thousands, the consumption of gas in cubic feet.

FIG. 296

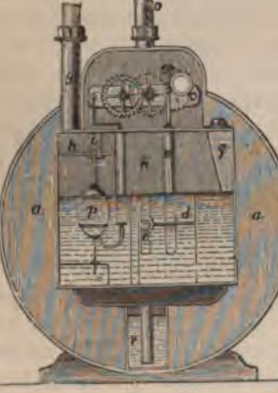
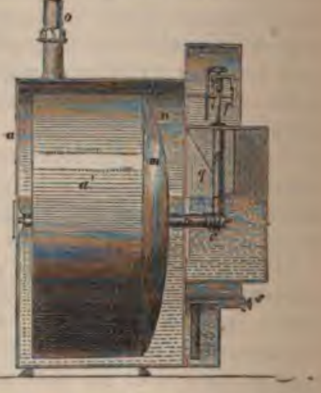


FIG. 297



Dry meters are preferred on account as well of not being liable to be affected by frost as of not causing the sudden extinguishing of the gas-lights for want of water, as may occur with wet meters. Wet meters are constructed upon a plan devised in 1817 by Clegg, and improved by Crossley and others. Figs. 296, 297, 298, and 299, are drawings of this kind of meter, which consists in the first place of an outer cylindrical box of cast-iron, closed on all sides. In this box is placed a drum of pure block-tin, divided into four compartments, bearing upon a bell-metal axis, and immersed for rather more than half its circumference in water. By the pressure of the gas and the ensuing depression of the water the drum revolves, each of its compartments becoming alternately filled with and emptied of gas. On the axis of the drum is an endless screw, which by mechanical means is connected with the wheel-work of the dials. The drum is very accurately adjusted, so that at every complete revolution a certain cubic quantity of gas passes through and is registered. Fig. 296 exhibits the apparatus with the front plate removed; Fig. 297 shows the side of the meter; Fig. 298 is sectional plan; and Fig. 299 is a section through the box. *a* is the box; *a'* the drum: *b* its axis; *c* the endless screw, bearing in the wheel, *d*, and carrying by means of *e* the movement of the drum on to the wheelwork of the dials, *f*. *g* is the inlet-pipe for the gas, which flows into the valve box, *h*, and passing by the valve, *i* (kept open as long as the meter contains sufficient water for its action), flows through the bent tube, *l*, into the bulged cover of the drum, or technically antechamber, *m*, and thence into the several compartments of the drum. Thence the gas enters the space, *n*, to which is fitted the outlet pipe, *o*. *i* is the valve; *p* the float; *q* the funnel tube for filling the meter with water; *r* the waste water cistern; *s* the plug by the removal of which the waste water may be run off. As long as no gas-burners are in use the meter connected with them is inactive, but when the gas is burnt the drum rotates, and by its communication with the wheelwork registers the quantity of gas consumed. Instead of filling wet meters with water they may be filled with glycerine, which does not freeze nor evaporate. Wet meters should be placed perfectly level. As regards their size they are made to supply from three lights up to many thousands if required. By an Act of Parliament gas-meters are tested in order to ascertain that they register properly within the limits of the Act. The inspectors of gas-meters have been provided with very accurate sets of apparatus made according to four sets of standard apparatus, of which one each is in the hands of the Corporations of London, Edinburgh, and Dublin; while the fourth is in the custody of the Comptroller of the Exchequer, at Westminster. These apparatus are masterpieces of highly finished workmanship.

FIG. 298.

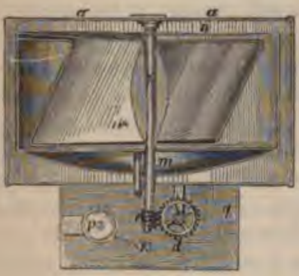
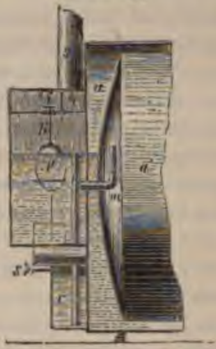


FIG. 299.



Burners. These are made so as to produce all shapes of flame, and are of different materials, iron, steel, porcelain, steatite, brass, platinum-lined, &c. The bore from which the flame of the burning gas issues should be arranged, as regards its width, for the quality of the gas consumed—cannel coal gas-burners, for instance, being provided with narrower openings than those for common coal-gas. We have single jet burners, double jet burners, bats'-wing, fish-tail, cockspur, and other varieties; also Argand burners of various sizes, bored with six to thirty or forty-eight holes, or as in the Dumas burner, a slit instead of the holes. The quantity of gas consumed by different kinds of burners varies, of course, greatly for the same kind of gas under the same pressure. Much gas is wasted because sufficient care is not taken by the consumers to have really good burners.

Gas Lamps. Of these there is an almost endless variety, from the most simple and unpretentious to the highly ornamented and expensive chandeliers.

By-products of Coal-gas Manufacture. Among these such as are of important commercial advantage to coal-gas works are:—1. Coke. 2. Ammoniacal liquor. 3. Tar. 4. Spent gas-lime. 5. Sulphur obtained from the Laming mixture. In some localities Berlin blue is made from the cyanide of calcium of the Laming mixture (see p. 656).

1. Coke, of which we shall speak more particularly under the heading of Fuel,

as gas-coke is more porous and spongy than the oven-coke and hence better adapted for use in stoves. In Germany the gas-works have now very generally adopted the plan of selling the coke broken up into small nut-sized lumps, this operation being performed by means of machinery; the breeze is mixed with some tar and burnt under the retorts at the works. 2. The ammoniacal liquor is essentially an aqueous solution of carbonate of ammonia, $2(NH_4)_2CO_3+CO_2$. The quantity of ammonia contained in this liquid must of necessity vary according to certain conditions, as the quantity of water contained in the coals, the larger or smaller amount of nitrogen they contain, the degree of temperature and duration of the process of distillation. The higher the temperature the more nitrogen will be converted into ammonia, while otherwise a portion of it is converted into aniline, lepidine, chinoline, &c., and also into cyanogen. Estimating gas-coals to contain on an average 5 per cent of hygroscopic water and 0·75 per cent of nitrogen, 100 kilos. of such coal will yield under the most favourable conditions 910 grms. of ammonia (NH_3). It has been found that 1 cubic metre of ammoniacal water yields on an average (see p. 230) 50 kilos. of dry sulphate of ammonia ($[NH_4]_2SO_4$), so that 20 hectolitres yield 100 kilos. of this salt. 1 ton of Newcastle gas-coal yields 45 litres of ammoniacal liquor, 1 litre of which yields from 74 to 81 grms. sulphate of ammonia. 3. Coal-tar, formerly a source of inconvenience to many gas-works, and at any rate a substance of very little commercial value, has become since 1858, of great importance as the raw material for the coal-tar colours. As already stated, tar consists of fluid hydrocarbons—benzol, toluol, propyl; solid hydrocarbons—naphthaline and anthracen; of acids—carbolic, cresylic, phlorylic; of bases—aniline, chinoline, lepidine, &c.; and lastly, of resinous, empyreumatic, and asphalte-forming matters. The quantity as well as the quality of the tar obtained by the distillation of coals for gas-making depends partly upon the kind of coal used and partly upon the heat applied to the retorts; as at a very high temperature, for instance with the fire-clay retorts, the quantity of tar is less than at a lower temperature. Owing as well to the carbolic acid contained in tar as to the empyreumatic substances, it has antiseptic properties, and is hence used for preventing the decay of wood exposed to wind and weather, for coating iron, &c. Coal-tar is also used for the purpose of mixing with small coal, saw-dust, peat dust, &c., for making artificial fuel, and recently, when mixed with sifted pebbles, as a substitute for asphalte to form excellent footpaths. In order to separate the constituents of tar from each other, it is poured into a large iron still, and heated to 80° to 100°, for the purpose of distilling off the light hydrocarbons along with any ammoniacal water the tar may contain. After thirty-six hours the distillation is further proceeded with, and as the latent heat of the volatile products to be obtained is very small, the still ought to be made as low as possible, and the helm ought to be well protected against any cooling influence. At the bottom of the still a tap is fitted for the purpose of removing, at the end of the distillation, the molten pitch which remains. In some cases, however, the distillation is pushed further so as to leave only a carbonaceous residue, the still being made red-hot at the bottom; the residue is removed after the cooling of the still by opening the man-hole. The distillation of 750 to 800 kilos. of tar takes twelve to fifteen hours. At first the heat should not be too strong, and in many tar distilleries high-pressure steam is passed through a coil of pipes placed in the still, in order to assist, together with open fire, the first stage of the distillation. The light tar-oils obtained exhibit first a sp. gr. of 0·780, but on an average 0·830. The heavy tar-oil comes over at 200°.

The light tar-oil is again distilled, and the distillate treated with strong sulphuric acid, next with caustic soda solution, and then again distilled. The treatment with sulphuric acid aims at the removal as well of basic substances (ammonia, aniline), as of naphthaline, while, by means of the caustic soda, the carbolic acid is fixed. The quantity of sulphuric acid to be used for this purpose amounts to 5 per cent of the weight of the tar-oil; while the soda solution of 1·382 sp. gr. (= 40° B.) amounts to 2 per cent of that weight. The liquid thus obtained is the benzol of trade; it remains colourless on exposure to air, and is a mixture of various substances with benzol, toluol, and xylol as chief constituents. It is easily converted into nitrobenzol (see p. 572), the starting-point for many of the coal-tar colours. The coal-tar naphtha, now usually sold after the benzol has been completely removed by fractional distillation, is used as a solvent for caoutchouc resins, fixed oils, gutta-percha, and for burning in lamps peculiarly constructed for the purpose, and only used in open air. Coal-tar naphtha is also used for carburetting gas of low quality. When the crude oil of tar is cooled down to −10°, naphthaline is deposited from it, which, as already mentioned (see p. 581), is used for the preparation of some dyes, and also for the manufacture of benzoic acid. The heavy oil of tar is purified with concentrated sulphuric acid and caustic soda ley, and freed from fœtid sulphur compounds by distillation over a mixture of sulphate of iron and lime. By fractional distillation between 150° and 200° creosote is obtained, being a mixture of carbolic or phenylic, cresylic, and phlorylic acids. This is the raw material used for the preparation of carbolic acid and picric acid (see p. 580), also for certain blue and red pigments, for creosoting wood, for preserving anatomical preparations, &c. Lunge obtained from a ton of tar:—

Benzol at 50 per cent	2·88 gallons	=	13·00 litres.
Best naphtha	2·69 „	=	12·00 „
Burning naphtha	3·51 „	=	15·08 „
Creosote	83·25 „	=	3·74 hectolitres.
Ammoniacal liquor	3·00 „	=	13·5 litres.

And 11¾ cwts. of pitch.

The heavy oils of coal-tar and the pitch are now largely used for the preparation of anthracen, from which artificial alizarine is made. The pitch is further usefully employed in lacquer and varnish making, and also for asphalting pavements. 4. The gas-lime is used abroad for the purpose of removing the hair from hides and skins intended to be tanned, the sulphuret of calcium contained in the lime acting as a depillatory. In some localities the spent lime is employed for making Berlin blue from the cyanide of calcium contained in the lime, and for the preparation of sulphocyanogen compounds, owing to the sulphocyanide of calcium it contains. As already mentioned, spent gas-lime is largely used in Scotland as a manure, which at the same time destroys a great many injurious insects. 5. Sulphur is prepared from the Laming mixture (see p. 198), and used for making sulphuric acid; it might, perhaps, be better to extract the sulphur from the mixture by means of steam at 130°. The Laming mixture is occasionally treated with heavy tar-oils for the purpose of eliminating the sulphur.

Composition of Coal-gas. The following figures exhibit the composition of purified coal-gas in 100 parts by bulk:—

	I.	II.	III.	IV.	V.	VI.	VII.
Hydrogen	44·00	41·37	39·80	51·29	50·08	46·0	27·7
Marsh-gas (methyl-hydrogen)	38·40	38·30	43·12	36·45	35·92	39·5	50·0
Carbonic oxide	5·73	5·56	4·66	4·45	5·02	7·5	6·8
Elayl	4·13	5·00	4·75	4·91	5·33	3·8	13·0
Ditetryl	3·14	4·34					
Nitrogen	4·23	5·43	4·65	1·41	1·89	0·5	0·4
Oxygen	—	—	—	0·41	0·54	—	—
Carbonic acid	0·37	—	3·02	1·08	1·22	0·7	0·1
Aqueous vapour	—	—	—	—	—	2·0	2·0

I. and II. Heidelberg coal-gas. III. Bonn coal-gas, analysed by H. Landolt. IV. and V. Chemnitz, Saxony, coal-gas analysed by Wunder. VI. London coal-gas (1867). VII. London cannel gas (1867).

Wood-gas. II. As already mentioned (p. 645) the French engineer Lebon was engaged in 1799 with the making of gas from wood, and brought out an apparatus termed by him a thermolamp, which, however, was neither found to answer for heating nor for illuminating purposes, as the illuminating power of the gas obtained by his process from wood was very inferior and could not compete with the coal-gas which became known soon after. The reason why wood, as converted into gas by Lebon's apparatus, did not give satisfactory results is explained by Dumas, by proving that under the conditions of the distillation of wood employed by Lebon, the gas evolved consists chiefly of marsh-gas and carbonic oxide, both of which can scarcely be considered luminous gases. In the year 1849, Dr. M. von Pettenkofer, at Munich, resolved to experiment on the manufacture of gas from wood, and he found that, as stated by Dumas, when wood is submitted to distillation in a manner similar to coal, the gas produced is entirely unfit for illumination, as in addition to carbonic acid, there are only formed carbonic oxide and marsh-gas. But Dr. Pettenkofer also found that when the vapours of tar and empyreumatic oils given off by the carbonisation of wood at a comparatively low temperature are further heated by passing through a red-hot retort, a very large quantity of heavy hydrocarbon gas remains among the products, so that then wood yields a better gas than coal.

While coals are not perceptibly acted upon by a temperature as high as 200°, wood gives off combustible vapours at 150°; and in order to understand the process of wood-gas manufacture, we must distinguish between the temperature at which wood is carbonised or converted into charcoal and empyreumatic vapours, and the temperature at which these vapours are converted into permanent gas suited for illumination. Coals, resin, and oils yield an illuminating gas at once, when submitted to dry distillation in gas retorts, because the temperature of carbonisation and of formation of gas are nearly the same; consequently the vapours formed by the dry distillation of these substances are far higher in illumination power than obtains in the case of wood. Therefore the apparatus in use for coal- and oil-gas preparation are not suited for making wood-gas. Some of the substances rich in carbon and hydrogen met with in wood-tar (Stockholm tar) boil, by themselves, at a higher temperature (200° to 250°) than that at which they are formed from wood; and the illuminating power of wood-gas is in a great measure due to their conversion, by a higher temperature, into permanent gases. The manufacture of wood-gas, therefore, requires in the first place a retort in which the wood is converted into vapour, and another retort or generator in which the vapours are rendered gaseous. At first the carbonising retort, of the same shape as the ordinary coal-gas retorts, was connected with a series of iron tubes, which were made red-hot, and through which the vapours given off by the carbonisation of the wood, at a temperature of 250° to 300°, were passed to be converted into gas: but now large retorts are used for this purpose, about three times as large as the carbonisation retort, which holds 60 kilos. of wood, and there is, therefore, ample space for the conversion of the vapours into gas. As regards the quality and quantity of gas obtained from different kinds of wood, there is no very great difference, as may be inferred from the under-mentioned results of the researches made by W. Reissig, who operated upon aspen wood (1); linden wood (2); larch wood (3); willow wood (4); fir-tree wood (5); and white wood or Memel timber (6).

50 kilos. (1) gave of purified gas 592 cubic feet, and 9·9 kilos. of charcoal.
50 „ (2) „ „ 620—640 „ „ 9—11 „ „
50 „ (3) „ „ 550 „ „ 12·5 „ „
50 „ (4) „ „ 660 „ „ 9·0 „ „
50 „ (5) „ „ 648 „ „ 9·5 „ „
50 „ (6) „ „ 564 „ „ 9·2 „ „

That the crude wood-gas contains a large quantity of carbonic acid may be inferred from the following results of analysis by Pettenkofer, the gas having been made of wood as much as possible free from resin:—

Heavy hydrocarbons	6·91
Marsh-gas (methyl-hydrogen) ...	11·06
Hydrogen	15·07
Carbonic acid	25·72
Carbonic oxide	40·59

One volume of the heavy hydrocarbons contained 2·82 volumes of vapour of carbon. The carbonic acid is removed from the crude gas by means of hydrate of lime. According to Reissig's researches, the composition of purified wood-gas is the following:—

	1.	2.	3.	4.
Heavy hydrocarbons	7·24	7·86	9·00	7·34
Hydrogen	31·84	48·67	29·76	29·60
Light hydrocarbon gas (marsh-gas) ...	35·30	21·17	20·96	24·02
Carbonic oxide	25·62	22·30	40·28	39·04
	100·00	100·00	100·00	100·00

Method of Wood-Gas Manufacture. The wood, chiefly fir-wood, is first dried for twenty-four hours in a drying room, generally brick-built, and heated by the waste heat of the retort furnaces. The carbonising retort is filled with 50 to 60 kilos. of wood and the lid screwed on; the distillation is finished in 1½ hours, and after the removal of the carbonic acid there is obtained about 16 cubic metres (nearly 600 cubic feet) of good illuminating gas. In some places, where wood-gas is regularly made, it is preferred to distil with the wood some Scotch boghead coal or Bohemian foliated coal (*Blattel kohle*).

Wood-Gas Burners. The construction of the burners is of great importance with regard to wood-gas illumination. The sp. gr. of this gas amounts on an average to 0·7, while that of ordinary coal-gas scarcely every reaches 0·5; the lighter the gas the more readily and rapidly it flows out and expands in the air, and the heavier the gas the more slowly and difficultly it issues and expands. A light gas will not on issuing into the air separate its particles, while, on the other hand, a heavy gas will, by exerting greater friction, mix with the air; in order that this effort shall not injure the luminosity or the gas, the openings in wood-gas burners must be considerably larger than in coal-gas burners. When wood-gas is burnt with rather strong pressure from coal-gas burners calculated to consume 70 to 100 litres (3 to 4 cubic feet) per hour, the flame is scarcely luminous, while when burnt from burners with large openings, wood-gas yields a light exceeding that of coal-gas. According to the experiments made in 1855 by Drs. Liebig and Steinhill, the illuminating power of coal-gas and wood-gas used each at 4½ cubic feet per hour was found to be:—

For coal-gas = 10·84 normal wax-candles.
„ wood-gas = 12·92 „ „ „

so that the average illuminating power of coal-gas stands to that of wood-gas as 6 : 5. The advantage of wood-gas manufacture over that of coal-gas (only of course in localities where wood is very abundant and coal either not to be had or at great cost) is evident enough, because, in addition to less complicated apparatus than required for coal-gas, the manufacture of wood-gas yields far more valuable by-products, wood charcoal being the chief of these. Wood, moreover, yields weight for weight more gas than coal in a shorter time and of higher illuminating power, while the gas is absolutely free from sulphur and ammoniacal compounds, so that by the burning of wood-gas no sulphurous acid can be formed. As the distillation of wood-gas proceeds rapidly, one retort kept continuously in action for twenty-four hours will yield 10,000 cubic feet, while for coal-gas only 4000 cubic feet are obtained with one retort in the same time. On the other hand, wood-gas requires for purifying purposes a very large quantity of quick-lime. The wood-tar, about 2 per cent of the weight of the dry wood, and the wood-vinegar—100 parts of wood yield 0·5 to 0·75 parts of dry acetate of lime—are usefully applied; the tar, however, is in some localities burnt under the retorts.

Peat-Gas. III. When peat is submitted to dry distillation, there is obtained, as with coals, an aqueous distillate, tar, and carbonised peat or peat-coke. Vohl obtained by the dry distillation of an air-dried peat, taken from a high moorland in the canton Zurich, Switzerland, from 100 parts:—

Gas	17·625
Tar	5·375
Aqueous distillate	52·000
Peat-coke...	25·000

The products of the dry distillation of peat are:—

Fluid and solid hydrocarbons.	Peat oil, 0·820 sp. gr. Heavy oil (lubricating-oil), 0·885 sp. gr. Paraffin.

Bases.
- Ammonia.
- Ethylamine.
- Picoline.
- Lutidine.
- Aniline.
- Cæspitine.

Acids.
- Carbonic.
- Sulphuretted hydrogen.
- Cyanhydric.
- Acetic.
- Propionic.
- Butyric.
- Valerianic.
- Carbolic.

Gaseous products.
- Heavy hydrocarbons.
- Light hydrocarbons.
- Hydrogen.
- Carbonic oxide.

The apparatus in use for making wood-gas answers the purpose of making peat-gas. W. Reissig, who has for a long time been engaged in experimenting on peat-gas manufacture, used a fat peat from the neighbourhood of Munich, containing very little ash and 14 to 15 per cent of water. On an average 1 Bavarian cwt. of this peat yields 426 Bavarian cubic feet of gas; 134 lbs. of this peat yield 337 English cubic feet of gas. The gas is evolved at first very rapidly, as is also the case with wood, but the evolution of gas from peat decreases more uniformly and steadily than it does from wood. Reissig's experiments prove that peat-gas may be prepared of very good quality; he found the purified peat-gas to consist of:—

I. Heavy hydrocarbons	9·52
Light hydrocarbon gas	42·65
Hydrogen	27·50
Carbonic oxide	20·33
Carbonic acid and sulphuretted hydrogen	traces
	100·00

The analysis of another gas, made with a very excellent peat, gave the following result:—

II. Heavy hydrocarbons $\left\{\begin{array}{l}\text{elayl,} = 9·52\\ \text{ditetryl,} = 3·64\end{array}\right\} =$	13·16
Light hydrocarbons	33·00
Hydrogen	35·18
Carbonic oxide	18·34
Carbonic acid and sulphuretted hydrogen	0·00
Nitrogen	0·32
	100·00

Water-Gas. IV. The manufacture of water-gas essentially consists in forcing steam through iron or fire-clay retorts filled with red-hot charcoal or coke. The steam is decomposed, yielding a mixture of hydrogen, carbonic oxide, and carbonic acid gases, with a small quantity of marsh-gas. The purified gas, consisting essentially of carbonic oxide and hydrogen, is, although not luminous when burnt by itself, suitable for illuminating purposes under the following conditions:—1. By placing on the burners small platinum cylinders which, by becoming white-hot, yield a strong light—Gengembre's and Gillard's plan. 2. By impregnating the gas with vapours of hydrocarbons, a more common plan, the original idea being due to Jobard (1832) of Brussels.

The determinations of the compositions of water-gas vary very much. Jacquelain and Gillard state that the crude gas obtained by them is a mixture of hydrogen and carbonic acid, which, after having been purified by means of lime, consists essentially of hydrogen. But it is stated by others, and not without good reason, that the purified gas contains carbonic oxide and hydrogen; and Langlois's results agree with this account. The formation of 1 molecule of carbonic oxide requires 1 molecule of steam, the hydrogen of which is set free, $C+H_2O=CO+H_2$. When the carbonic oxide meets again with steam at a higher temperature, it, as has been experimentally shown by Dr. Verver, withdraws oxygen from the steam, forming carbonic acid, while some hydrogen is again set free: $CO+H_2O=CO_2+H_2$. Only when the carbonic acid is not withdrawn rapidly enough from the retorts is its re-conversion into carbonic oxide by contact with the red-hot charcoal possible.

Gillard's Gas. Platinum Gas. In the year 1846, Gillard established at Passy, near Paris, a gas-work for the purpose of manufacturing hydrogen by the decomposition of water. At first the steam was decomposed by passing it through retorts filled with ret-hot iron wire, the idea being to re-convert the oxidised iron to the metallic state; but as this process did not answer, Gillard commenced decomposing the steam by passing it through a retort filled with red-hot charcoal. The crude gas thus obtained is readily freed from the large quantity of carbonic acid it contains, by crystallised carbonate of soda, which is converted into bicarbonate of soda. The gas is burnt from an Argand burner provided with numerous small holes, and the flame, not luminous by itself, is surrounded by a net-work of moderately fine platinum wire, which on becoming white-hot is luminous. In Paris this gas is known as platinum-gas (*gaz-platine*). It is free from smell, burns without smoke or soot, and for this reason is preferred by gold and silversmiths and electro-gilders. The illuminating power of this gas exceeds that of coal-gas in the proportion, according to Girardin, of 130 : 127. The flame is quite steady, because the light-producing substance is a solid body at a white heat.* According to Dr. Verver's researches there are used at Narbonne, France, for the production of 1 cubic metre of this gas 0·32 kilo. of wood-charcoal, and for heating the retorts 1·41 kilos. of coals.

Carburetted Water-Gas. While engaged in his experiments on the oil obtained by the strong compression of oil-gas, Faraday proved that if marsh-gas, which burns with a scarcely luminous flame, is impregnated with this oil, it becomes a very luminous gas. Lowe proposed, in the year 1832, that common coal gas should be rendered more luminous by impregnating it with vapours of tar-oil or petroleum. He also showed that with the aid of steam and red-hot coke a mixture of carbonic oxide and hydrogen might be obtained and rendered luminous by impregnation with these vapours. Afterwards Jobard, at Brussels, took up the subject and communicated his researches to the French gas-engineer Selligue, who having at an earlier period (1833) been engaged with similar researches, entered upon the subject with great energy, and employed carburetted water-gas for illuminating purposes on the large scale. Selligue used the oil obtained from a bituminous shale for the purpose of carburetting the water-gas, the oil being obtained in the same manner as such oil is now made from various kinds of cannel coal and bituminous shales. Selligue's gas-making apparatus consisted of a battery of three vertical retorts kept continuously red-hot, two of these retorts being filled with charcoal or coke of good quality and very free from sulphur. Into the first of these retorts, which are connected together, steam is introduced, forming with the red-hot charcoal carbonic oxide and hydrogen. This gaseous mixture passing through the second retort, also filled with charcoal, is there deprived of any carbonic acid, which is converted into carbonic oxide. This is the reverse of the method of water-gas making now employed, where the carbonic oxide is converted into carbonic acid, to be next removed from the gaseous mixture by means of lime. The very hot mixture of hydrogen and carbonic oxide is next passed into the third retort, which is filled for two-thirds of its height with iron chains kept red-hot, while a continuous stream of the oil of the bituminous shale flows from a reservoir through a syphon-pipe into this retort (to every 10,000 litres of gas 5 kilos. of oil are admitted), and upon becoming decomposed, mixes with the carbonic oxide and hydrogen, forming a gaseous mixture, which, notwithstanding the large quantity of carbonic oxide contained, burns with a highly luminous flame, the gas being at the same time of great durability. A gas-furnace upon Selligue's plan and containing six retorts in two batteries, together of 6 cubic metres capacity, yielded in twenty-four hours 24,000 to 28,000 hectolitres (=84,768 to 98,896 English cubic feet) of excellent gas, with a consumption of 1231 kilos. of oil of bituminous shale, 400 kilos. of wood-charcoal, and 16 hectolitres of coal for firing the retorts.

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* Schinz has lately published an essay on this gas; see Dr. Wagner's "Jahresbericht der chem. Technologie," 1869, p. 731.

Selligue's process has given rise to the following methods:—1. White's hydrocarbon process, in which steam and gas are made from coals (originally resin was employed, but cannel coals have been substituted) under the influence of a jet of superheated steam passed through a red-hot retort. 2. Leprince's process, *Gas mixte Leprince*, is an improved hydrocarbon process, the products of the decomposition of steam and coke being carried at a suitable temperature and in the same retort (provided with a partition and thus divided into two compartments) over coals in process of carbonisation. 3. Isoard's process, with superheated steam and coal-tar mixed. 4. According to Baldamus and Grüne's plan, steam and a fluid hydrocarbon are decomposed simultaneously in the same retort. 5. Kirkham's plan and that of others, the impregnation of water-gas with fluid hydrocarbons, benzol, photogen, petroleum, naphtha, &c. 6. Longbottom's proposal to carburet air by impregnating it with vapours of benzol, or, according to Wiederholt's plan, with petroleum naphtha, the benzoline as used in sponge-lamps.

White's Hydrocarbon Process.

White in so far modified Selligue's plan in causing water-gas and steam to be forced through a retort in which cannel coal, boghead, or resin are submitted to distillation. White's process, as yet rarely employed, came under notice through the researches which Dr. Frankland instituted at Clarke and Co.'s gas-works at Ancoats, near Manchester.

Dr. Frankland found the gas made by White's process to contain about 15 per cent of carbonic oxide, no carbonic acid, and some 45 per cent of hydrogen. This increase of hydrogen, without an equivalent increase of carbonic oxide, can only be explained by the action of the steam upon the marsh-gas evolved in the retort filled with cannel coal, probably according to the following formulæ:—

$$\left.\begin{array}{l}\text{Marsh-gas, } CH_4\\ \text{Steam, } H_2O\end{array}\right\}\text{ yield }\left\{\begin{array}{l}\text{Carbonic oxide, } CO.\\ \text{Hydrogen, } 3H_2.\end{array}\right.$$

The composition of the gas, made with and without water-gas, was as follows:—

Gas from Boghead coal:—

	Without water-gas.	With water-gas.
Heavy hydrocarbons	24·50	14·12
Marsh-gas	58·38	22·25
Hydrogen	10·54	45·51
Carbonic oxide	6·58	14·34
Carbonic acid	—	3·78
Oxygen and nitrogen	—	—
	100·00	100·00

The advantages of White's hydrocarbon process are not only the increase of hydrogen and decrease of carbonic oxide and marsh-gas as met with in ordinary coal-gas, but are to be found in the mechanical action of the products of the decomposing steam by carrying off very rapidly the heavy hydrocarbons from the retort, so that these are withdrawn in time from the decomposing influence of high temperature, thereby lessening the formation of tar. Dr. Frankland summarises the results of this process as follows:—*a*. It can be employed without great expense in any gas-work. *b*. The quantity of gas yielded increases from 46 to 290 per cent. *c*. The illuminating power increases from 14 to 108 per cent. *d*. Less tar is made, a portion being converted into gas. *e*. The heat and formation of carbonic acid accompanying the combustion is much less, as this gas contains more hydrogen and less carbon.

Leprince's Water-Gas. This is only a modification of White's process, consisting chiefly in the use of retorts divided by means of horizontal partitions into three rooms or chambers, in which the two phases of the process, viz., the partial decomposition of water by means of coke or charcoal, and the carburation of the gas by means of the volatile products of the dry distillation of gas-coals, are carried on simultaneously. The *Gas mixte Leprince* is used in the broad-cloth factory of Simonis at Verviers, and at the Vieille Montagne zinc-works, both in Belgium, also at Maestricht and some places near Luik Liège.

Isoard's Gas. In this process tar is used instead of charcoal or coke for the purpose of decomposing the steam.

Baldamus and Grune's Gas. According to this plan the decomposition of steam and of the hydrocarbons is carried on simultaneously in the same vessel, so that the hydrogen contained in the steam is not evolved in free state, but in combination with carbon as a light-giving hydrocarbon. The gas-making material, brown coal, peat, bituminous shale, &c., is fully utilised without any by-products, for the tar is entirely converted into gas, forming with the hydrogen of the water a real hydrocarbon.

Carburetted Gas. The process proposed by Kirkham and several others simply consists in the impregnation of water-gas with the vapours of fluid hydrocarbons, benzol, photogen, petroleum, &c. This impregnation may take place at the works where the gas is made, but better where the gas is consumed, just before issuing from the burners. Notwithstanding that a great many apparatus have been contrived for the purpose of carburetting water-gas and ordinary coal-gas, the process has never answered very well, because it is difficult to find suitable materials for carburetting, and because erroneous calculations have been made in respect of the quantity of carburetting materials required to render a non-luminous gas luminous. If, for instance, benzol (C_6H_6) be the hydrocarbon to be used for carburetting purposes,

$$1000 \text{ cubic feet of gas require} \left\{ \begin{array}{l} \text{at } 0^\circ, 2342 \text{ grms.} \\ \text{,, } 15^\circ, 5694 \text{ ,,} \end{array} \right\} \text{benzol.}$$

The improvement of coal-gas by impregnating it with the vapours of some volatile hydrocarbon has been frequently suggested and practically tried in England; but, although various apparatus have been contrived for this purpose, such apparatus being generally fixed to the outlet-pipe of the house-meters, the results have not been so satisfactory as to lead to a general introduction of these so-called carburetters. Among other reasons why these appliances have been discarded, is the fact that the gas, especially in London, contains sulphuretted hydrocarbon compounds in very small quantity, which, by becoming dissolved in the hydrocarbon used for impregnating the gas, accumulate in the carburetter, and are, when fresh carburetting oil is added, carried on to the burners and escape partly in the state of vapour, causing a very foul atmosphere in the rooms where the gas is burnt.

Air-Gas. Longbottom suggested to free air from carbonic acid and moisture, and then to impregnate it with the vapours of very volatile fluid-hydrocarbons, such as benzine and benzoline. Air can be used as an illuminating gas in this way, but it requires burners with wide openings and a low pressure, because if the current of the gas be too rapid the flame is cooled too much and readily extinguished. Apparatus for preparing air-gas have been devised and constructed by Marcus, Mille, Methei, and others.*

Oil-Gas, Resin-Gas. V. The fatty, or so-called fixed oils, are among the best gas-making materials, yielding a very pure gas and of high illuminating power. This follows from their composition:—Lefort found the formula of rape-seed oil to be $C_{10}H_{18}O_2$; olive oil and poppy-seed oil, $C_{18}H_{32}O_2$; linseed oil, $C_{15}H_{28}O_2$; hemp-seed oil, $C_{11}H_{22}O_2$. The fatty oils yield by dry distillation chiefly elayl-gas or a mixture of hydrogen and marsh-gas with the vapours of fluid hydrocarbons, the illuminating power of which is equal to that of elayl-gas. As oils yield further only a small quantity of carbonic acid gas and no sulphuretted hydrogen, oil-gas does not require any purifying, and hence the apparatus may be very simple; while, owing to the high illuminating power, smaller gas-holders, smaller pipes, and burners of different construction are required. But notwithstanding all these advantages, oil-gas is a thing of the past. The Binnenhof, at the Hague, with some of the adjacent public buildings, was lighted with oil-gas until within some ten or twelve years, when the apparatus requiring renewal was removed, and coal-gas, as in the other parts of the town, substituted. The sp. gr. of oil-gas amounts on an average to 0·76 and 0·90, but may be as high as 1·1. Half a kilo. of oil yields 22 to 26 cubic feet of gas, equal to 90 to 96 per cent.

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* See "Jahresbericht der chem. Technologie," 1866, p. 701; 1868, pp. 763 and 765.

Gas from Suint. By this we understand a gas prepared from the fatty materials present in the soap-suds used in washing raw wool and spun-yarns. The water containing the suint and soap-suds is run into cisterns and is there mixed with milk of lime and left to stand for twelve hours. A thin precipitate is formed, which, after the supernatant clear water has been run off, is put upon coarse canvas for the purpose of draining off any impurities, sand, hair, &c., while the mass which runs through the filter is put into a tank, in which it forms after six to eight days a pasty mass, which having been dug out and moulded into bricks, is dried in open air. At Rheims the first wash-water of the wool is used for making both gas and potash, because the water contains no soap and only suintate of potash (see p. 132). Havrez, at Verviers, has recently proposed to employ suint, which, by-the-bye, is very rich in nitrogen, for the purpose of making ferrocyanide of potassium.

The dried brick-shaped lumps are submitted to distillation, yielding a gas which does not require purification, and which possesses an illuminating power three times that of good coal-gas. The wash-water of a wool spinning-mill with 20,000 spindles yields daily, when treated as described, about 500 kilos. of dried suinter, as the substance is technically termed. 1 kilo. of this substance yields 210 litres of gas. Annually about 150,000 kilos. of suinter are obtained, and this quantity will yield 31,500,000 litres = 1,112,485 cubic feet of gas. Every burner consuming 35 litres of gas per hour, and taking the time of burning at 1200 hours, the quantity of gas will suffice for 750 burners, and as a spinning-mill of 20,000 spindles only requires 500 burners, there is an excess of gas supply available for 250 other burners, or the owner may dispose of 5000 kilos. of suinter, which is valued at Augsburg at about 3s. per 50 kilos., and at about 4s. at Mulhouse.

Gas from Petroleum Oil, or Oil from Bituminous Shales. VI. The so-called posidonian schist of the lias formation, met with near Reutlingen, in Würtemberg, yields by dry distillation about 3 per cent of tar, which on being submitted to distillation, yields an oil which cannot be burned in lamps owing to its containing sulphur; but the oil is an excellent material for gas manufacture, According to Haas, 1 cwt. (50 kilos.) of the oil, valued at 16s., yields 1300 English cubic feet of gas, so that 1000 cubic feet inclusive of fuel ($\frac{1}{12}$ klafter of wood; the klafter is a cubic measure by which wood is sold, and is = 108 cubic feet) and labour cost 16s., a low price considering the high illuminating power of the gas. The gas, according to W. Reissig's researches (1862) was found to consist of:—

Heavy hydrocarbons	25·30
Marsh-gas	64·80
Carbonic oxide	6·65
Hydrogen	3·05
Carbonic acid	0·20
Oxygen and nitrogen	traces
	100·00

According to experiments made at Stuttgart, the illuminating power of this gas is 2·5 to 3·5 times that of coal-gas.

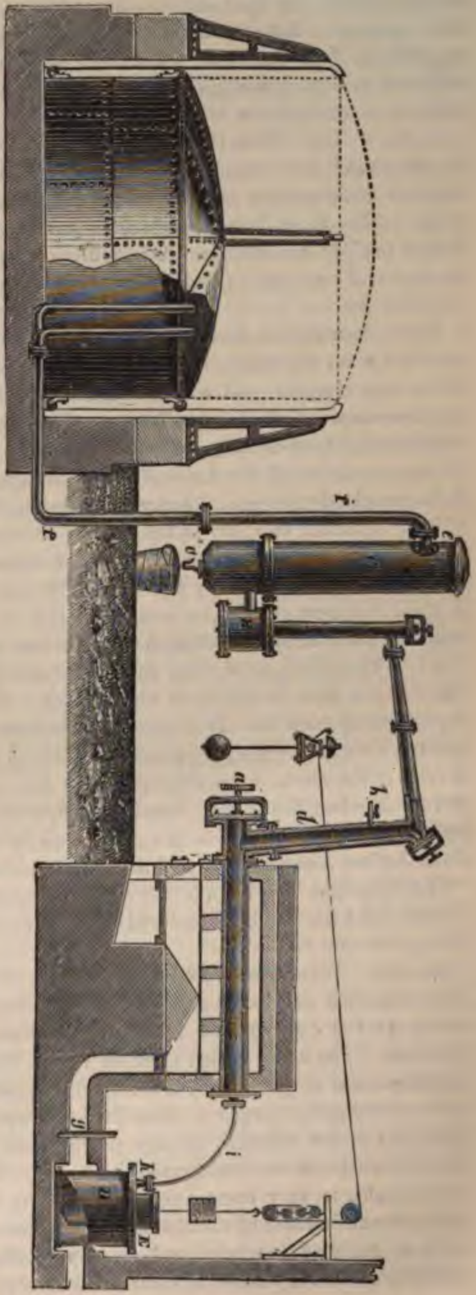
Petroleum-Gas. In America and on the Continent of Europe petroleum is now used for the purpose of gas-making, being either converted into gas or used to carburate water-gas.

According to the method of Thompson and Hind (1862) the petroleum is converted into gas by causing it to pass through a red-hot retort, which, in order to increase the contact surface, is filled with lumps of fire-brick or is fitted with a series of tray-like iron plates, and the gas so obtained mixed with that made by passing steam over red-hot charcoal. The crude gaseous mixture is washed by causing it to bubble through hydrochloric acid and then through a series of purifying apparatus, so that the gas collected in the gas-holder is devoid of smell. The arrangement of the retort used in this process is the following:—The retort is placed horizontally; to the lid is fitted a hollow cylinder which is filled with coke or charcoal. In the space between this cylinder and the sides of the retort is placed a serpentine iron plate. Through the lid of the retort two tubes are carried; one of these, communicating with the serpentine iron plate, is destined for the introduction of the petroleum oil, while the other is used for passing in the steam, and communicates with the cylinder filled with coke or charcoal. At the other end of the retort a tube is fitted for carrying the gas to the purifier. When the petroleum is converted into gas without water-gas, 1 cwt. of Pennsylvanian oil yields 1590 cubic feet of gas, which, when purified, consists, according to Bolley, of:—

	I.	II.
Heavy hydrocarbons	31·6	33·4
Light hydrocarbons	45·7	40·0
Hydrogen	32·7	26·0
	100·0	100·0

H. Hirzell prepares gas from the residues of the refining of petroleum, which are less volatile, as well as from petroleum itself. Hirzel's apparatus, already largely used in Germany, Austria, Russia, and elsewhere, is especially adapted for the purpose of making gas for railway-stations, barracks, factories, hotels, and isolated country seats; its mode of action will be readily understood with the aid of Fig. 300. D is a wrought-iron vessel containing petroleum or the residues of the refining. This vessel is fitted with a suction- and force-pump, E, the piston of which can be filled with petroleum by winding up the clockwork with which it is connected. As soon as the retort is red-hot, weights are put on the piston, after which the pendulum of the clockwork is set in motion and the rope unreeled, allowing the piston to sink slowly into the pump-body, thus forcing the petroleum through *i* uniformly into the retort A. The petroleum is converted into gas, and this is carried through the tube *d* into the receiver, B, and thence through the condenser, C, which is filled with pieces of brick, into a gas-holder. In B the pipe dips under the surface of the petroleum, so that a hydraulic valve is provided, preventing the gas from returning to the retort. In order to keep this column of petroleum at the same height, there is fitted to *e* the U-shaped tube *c*, by means of which any superfluous oil entering *c* is run off into a pail. The tube *b*, fitted to the gas-tube *d*, is, by means of a pipe, connected with a water-pressure gauge, by the aid of which the pressure in the retort during the operation can be ascertained; this pressure amounts usually to 8 to 12 centims. of water. The lid, *e*, of the condenser, C, is kept gas-tight by the rim dipping in water poured into an annular space. The working of this apparatus is very simple. The clock-motion is maintained for an hour, and in that time about 200 cubic feet of gas are made. If by any chance the tubes are choked, the manometer will indicate the accident. When in regular use the apparatus should be cleaned once in five or six weeks, and after every twelve distillations the retort should be opened and the crust of coke picked off with a sharp iron bar. Petroleum-gas is the best that can be made, and it has the advantage that even under strong pressure and intense cold it does not deposit tarry matter, nor does it lose any of its illuminating power. It is absolutely free from ammoniacal and sulphur compounds and from carbonic acid. The sp. gr. of petroleum-

FIG. 300.



gas is 0·69, and it consists chiefly of acetylen (C_2H_2). It is burnt from burners which consume per hour only one-quarter of a cubic foot to a maximum of 2 cubic feet. 200 cubic feet of this gas are equivalent to 1000 cubic feet of coal-gas. At the suggestion of L. Ramdohr (1866), the sodium carbolate (creosote soda), which is obtained in large quantities in the paraffin and mineral-oil works, is used for gas-making under the name of creosote-gas.

Resin-Gas. VII. When the substance known as Venice turpentine, a mixture of oil of turpentine and resinous matter, is submitted to distillation with water, there remains colophonium, or commonly resin, which essentially consists of sylvic and pinic acids, these being isomeric and corresponding to the formula $C_{20}H_{30}O_2$. Before the late American war colophonium was imported in very large quantity into Europe, and was used in England as well as on the Continent for the purpose of gas manufacture.

When decomposed under the influence of heat colophonium yields an oily fluid, so-called resin oil, which, when submitted to red-heat, is converted into gas. This oil is very complex, and contains bodies which are volatilised below red-heat, an inconvenience in gas-making, because these compounds as soon as formed become volatilised instead of being converted into gas. Consequently it is necessary to pass the first products of the decomposition through several retorts in order to convert them completely into gas, thereby complicating the apparatus and increasing the cost of fuel. Another difficulty in the making of resin-gas is occasioned by the fact that colophonium is a solid substance which, in order to be fitted for gas-making, so as to supply the retorts uniformly and constantly, has to be first liquefied. This has been in some instances effected by dissolving the resin either in oil of turpentine or in resin oil, while in other instances the resin has been first molten, and then caused to flow into the retorts filled with coke or lumps of fire-brick to increase the surface. The hot gas from the retorts is washed with cold water in order to free the gas from any adhering resin oil. It is next purified from the carbonic acid it contains (on an average about 8 per cent) by passing it through a solution of caustic soda. 100 lbs. of resin yield about 1300 English cubic feet of gas, a quantity which is greatly increased when the White-Frankland hydrocarbon process is employed. This process, however, is obsolete in consequence of the very fluctuating supply of resin since the last American war and the greatly increased price of that article.

The lime-light, Tessié du Motay's oxyhydrogen light, the magnesium light, and the electric light have to be considered as appendices to the illuminating and artificial light producing materials.

Lime-Light. When a mixture of two volumes of hydrogen and one volume of oxygen is ignited, each gas being supplied from a separate gas-holder, we obtain what is known as the oxyhydrogen blowpipe, the heat evolved being sufficient to fuse platinum. The flame of this mixture is not luminous, but if it is made to impinge against a piece of quick-lime, the latter being rendered intensely white-hot, emits a light of very great intensity. For the general purposes of artificial illumination the lime-light is not suitable, arising partly from the high price of oxygen; but for scientific purposes and for signals, the lime-light, also known as the Drummond-, or sideral-light, is very manageable. According to the "Journal of Gas Lighting" (1869) the authorities of the British War Department have arranged to use the lime-light in military barracks and cavalry stables, having instituted a series of experiments in the yard of the Queen's Barracks. The illuminating apparatus and reflecting mirror were placed on a temporarily-erected wooden frame-work, 18 feet high, and when the lime was ignited the yard was lighted up so strongly, that at 100 yards distance from the light the smallest type could be read. A smaller light surrounded by a glass globe was tried, and found to be so efficient, that at 30 yards distance from the light a pin could be distinguished lying on the pavement. The light-apparatus tried in one of the barrack-rooms was still smaller, but lighted the room very brilliantly.

Tessié du Motay's Method of Illumination.

For some years Tessié du Motay's method of illumination has been often before the public. During the latter part of 1871 and the earlier months of this year, this method has made considerable progress in improvement, and is used in some parts of Paris and Vienna, and has been tried at the Crystal Palace. The gas-mixture used is either water-gas—a mixture of hydrogen and carbonic oxide—or hydrogen only, or also coal-gas, burnt with a regulated supply of oxygen instead of air. The oxygen is obtained by the decomposition of the vapours of sulphuric acid or from manganate of sodium, or by the decomposition of oxychloride of copper. The flame of the oxyhydrogen gas is made to play against a small cylindrical piece of magnesia or zirconia; but more recently (1869) Tessié du Motay has somewhat altered his method, by causing the oxygen to become saturated with a solution of naphthaline in petroleum. It appears that the latest and most practically available method is the feeding of good coal-gas with oxygen, a very excellent light being produced.

Mr. Crookes has found a supply of good coal-gas best adapted to the oxy-hydrogen flame, the oxygen being supplied from a burner quite separate from the hydrogen burner, and having a broad slit from which the gas issues. The oxygen should be supplied at a steady but full pressure. The material upon which the flame impinges may, with advantage, be of dolomite. Under these conditions, Mr. Crookes has always found the lime-light to work satisfactorily. The dolomite does not crack nor splinter, as is the case with quick-lime or magnesia. There are also the advantages in employing separate burners, of decreased expense of apparatus, and of perfect safety.

MM. Deville and Gernez proposed some time since to make a series of experiments to ascertain, in a chamber containing compressed air, whether the tension of steam (which is said to be complementary to the tension of dissociation) in the flame of the oxyhydrogen blowpipe is augmented by exterior pressure, and if the augmentation extends to the temperature of the flame. In a cylindrical chamber of forty metres contents, and the sides of which have been proved to eleven atmospheres, is arranged the necessary apparatus. The operators enter the cylinder, and the air is compressed by means of a steam-pump, when the experiments are proceeded with as in the open air. The endeavour has at present been confined to ascertaining the condition of various substances at the moment they combine in homogeneous flames, and the resulting temperatures. The homogeneous flame employed is that of carbonic oxide and oxygen. With this flame and a pressure of 1·7 atmospheres platinum melts, flying off in sparks with a facility it never exhibits in air; it melts in those portions of the flame which in the air would only heat it to redness. We must then deduce that the temperature of these flames augments with the pressure they support, and, consequently, the quantities of matter which combine are greater, and the dissociation diminished. Dr. Frankland has shown that the brilliancy of the flame of hydrogen gas increases considerably with the pressure, so that with a pressure of twenty atmospheres it surpasses that of a normal candle. Similarly when a mixture of oxygen and hydrogen is ignited in an eudiometer the flame is intense, while in open air it is scarcely visible. M. Deville thinks that if the quantity of heat disengaged by a substance burning with brilliancy be measured, the result would not be the same in operating with an opaque calorimeter as with one which transmits the light and chemical rays. This remark when worked out will probably produce results of technical interest.

Magnesium Light.

The very intense light which is produced by the burning of magnesium (see p. 114) has been of late frequently employed for photographing purposes. Magnesium lamps—as exhibited in 1867 at the International Exhibition, at Paris—

are arranged for the use of magnesium wire or magnesium dust, while in each instance a spirit-flame is employed to ensure the continuity of combustion. In the lamps with wire, this is pulled forward by the aid of clockwork; while in the lamps burning the dust, this, mixed with very dry and fine sand (one-third magnesium and two-thirds sand), in order to ensure to the magnesium particles a sufficient access of air, is, on opening a stop-cock, supplied from a reservoir. The magnesium light was used on a large scale in the Abyssinian war, several cwts. of magnesium having been supplied by Mr. Mellor, the director of the Magnesium Metal Company, at Manchester.

Chatham Light. Under this name is known in England a kind of flash-light, obtained by blowing a mixture of pulverised resin and magnesium dust through the flame of a spirit-lamp. This flash-light is used for military signals.

Electric Light. Although the electric light has not been generally employed it deserves a lengthy notice. As is well known, the discharge of an electric spark, or a continuous voltaic or magneto-electric current, is capable of producing in pieces of graphite an intense light; and when this is obtained by suitably constructed apparatus, it may be rendered available for practical purposes. More recently Professor Jacobi has, with the assistance of M. Argeraud, of Paris, made a series of experiments on street lighting with the electric light. Upon the tower of the Admiralty buildings at St. Petersburg, an electric light apparatus was placed, and with it three of the largest streets of the city, viz. Newsky Prospect, Erbsen Strasse, and Wosnesensky Prospect, were illuminated at night from seven until ten o'clock. The light was intense, and the very clear sky appeared as by sunlight, while the gaslights became lurid. The battery employed was a carbon battery of 185 cells. In 1854, the works for the construction of the Napoleon docks, at Rouen, were for several nights illuminated with the electric light for three to four hours consecutively; 800 men were at work, and could continue their labour at a distance of 100 metres from the source of light. A Bunsen battery of large size with 100 cells was used. This light was very cheap, the cost per man being about three farthings; while the labour could proceed as in daylight. Several lighthouses, among them the North Foreland on the Kentish coast, and also that of Cape la Hève near Havre, have been fitted with apparatus for the electric light. This light is also used in many cases in dissolving views, and for the illumination of pleasure gardens at London, Paris, Berlin; and permanently for lighting the slate quarries situated near Angers, France. The electric light has been tried for submarine illumination with success, and also for photographing purposes. Colonel von Weyde invented a submarine electric illuminating apparatus, used by the French men-of-war in the late conflict between France and Germany. In Spain, in 1862 and 1863, the electric light was frequently employed during the night in the construction of railways. The magneto-electric apparatus invented by Dr. Siemens (1867) is of great importance, as proved by the experiments made at Burlington House. By means of this machine it becomes possible to obtain electric currents at a cheap rate, of enormous power, and especially adapted for lighthouses.

By the exercise of great ingenuity, the difficulties attending the maintenance of the carbon points at an equal distance have been overcome. The lamps in which this result is effected are, however, more or less complicated, expensive, and liable to get out of order. The electric lamps of Foucault, Serrin, and Duboscq, described admirably in Dr. Schellen's "Spectrum Analysis," and engravings of which are to be met with in most treatises on physics, are delicate pieces of mechanism peculiarly unsuited to the rough handling to which apparatus in use for technical or signalling purposes must be submitted. The electric lamp devised by Mr. Browning is simple in construction, but even this requires more attention than could be bestowed upon the source of light for general purposes.

The purity of the carbon points has much to do with the intensity of the light emitted by batteries of the same strength; while their distance from each other is also of consequence. 50 or 60 Bunsen's elements will yield a light equal to that of 400 to 1000 stearine candles, according to the purity of the carbon points. Taking the sunlight at noon on an August day to be represented by 1000, Foucault and Fizeau have found the chemical power of the light obtained, under the best conditions, from 46 Bunsen's cells, expressed by the number 235. Despretz states that the light from 100 Bunsen elements produces much discomfort to the eyes, while that from 600 elements, even at a glance, is sufficiently intense to cause considerable injury. But the duration of the electric light as obtained from battery power is not continuous. Whether from polarisations in the battery or from many other causes, the light sometimes fails for several consecutive minutes. It becomes then necessary to have recourse to some source of electricity in which these objections are eliminated. To a great extent this is the case with magneto-electricity. The light from Messrs. Wilde's large machine is the most powerful artificial light which has ever been produced, giving about eight times the light of former magneto-electric machines. Like most practical applications of science, the important results which Mr. Wilde has obtained depend more upon an ingenious combination of several known facts, united with considerable engineering skill, than upon any really new and striking discovery. The principle of the machine can be expressed in a few words. It consists in the application of a current from an electro-magnetic machine, armed with permanent magnets, for the purpose of exciting a powerful electro-magnet; this electro-magnet being now used as the basis of a still larger electro-magnetic machine, for the purpose of having induction currents generated by its agency. In other words, by well-known means, an electric current can be obtained by the rotation of an armature close to the poles of a magnet. If this electric current be passed round an electro-magnet, it may be made to produce a far greater amount of magnetism than was possessed by the first magnet. There is no difficulty, therefore, in comprehending how, by the mere interposition of a rotating armature, and the expenditure of force, a small and weak magnet may be made to actuate a very powerful magnet. But as the power of the magnet increases, so does the power increase of the electric current which may be generated by induction in an armature rotating between its poles. We have, therefore, only to pass this No. 2 induced current from No. 2 magnet round a still larger magnet, No. 3; and by rotating an armature between its poles, we can get a still more energetic current, No. 3. Theoretically there is no limit to this plan—it is a species of involution; and when it is considered that each conversion from magnet No. 1 to magnet No. 2, &c., or from induced current No. 1 to induced current No. 2, &c., multiplies the power very many times, it will not be surprising that after three involutions the induced current possesses such magnificent powers.*

Some erroneous opinions are pretty generally entertained as to the actual discovery claimed by Mr. Wilde, and the splendour of the result, for achieving which he deserves the very highest credit, is liable to cause earlier investigators in the field to be overlooked; this would be most unfair, for it is through their instrumentality that the way has been paved for the success now achieved. In 1838, Abbés Moigno and Raillard proved that by taking an electro-magnetic machine, the original magnet of which would support only a few grammes, and passing the electric current generated by it round a large electro-magnet, the latter could be made to support a weight of 600 kilogrms. The Abbés carried the multiplication of power only so far as to obtain the more powerful magnet, No. 2, from the weak magnet, No. 1.

With the three armatures of Mr. Wilde's machine driven at a uniform velocity of 1500 revolutions per minute, an amount of magnetic force is developed in the large electro-magnet far exceeding anything which has hitherto been produced, accompanied by the evolution of an amount of dynamic electricity from the quantity armature so enormous as to melt pieces of cylindrical iron rod fifteen inches in length and fully one quarter of an inch in diameter. With this armature in, the physiological effects of the current can be borne without inconvenience. When the intensity armature was placed in the 7-inch magnet cylinder, the electricity melted 7 feet of No. 16 iron wire, and made a length of 21 feet of the same wire red-hot. The illuminating power of the current from this armature was of the most splendid description. When an electric lamp, furnished with rods of gas carbon half an inch square, was placed on the top of a lofty building, the light evolved from it was sufficient to cast the shadows of the flames of the street lamps a quarter of a mile distant upon the neighbouring walls. When viewed from that distance, the rays proceeding from the reflector have all the rich effulgence of sunshine. With the reflector removed from the lamp, the bare light is estimated to have an intensity equal to 4000 wax candles. A piece of ordinary sensitised paper, such as is used for photographic printing, when exposed to the action of the light for twenty seconds, at a distance of 2 feet from the reflector, was darkened to the same degree as a piece of the same sheet of paper was when exposed for a period of one minute to the direct rays of the sun at noon on a very clear day in the month of March. Paper could be easily set on fire with a burning-glass introduced in the path of the rays from the reflector.

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* See "A New Era in Illumination," by W. Crookes, F.R.S.; "Quarterly Journal of Science," October, 1866.

It will be of interest, apart from all questions as to economical production, to ascertain what is the theoretical quantity of coal required to be consumed in the production of this amount of electric force. Mr. Wilde says that a 7-horse engine is required to drive the machine. One horse-power is equal to 1,980,000 foot-pounds per hour; that multiplied by seven is 13,860,000 foot-pounds per hour, which therefore represents the actual power required to drive the machine. Now, by multiplying the British Fahrenheit units of heat produced by the combustion of one pound of coal by Joule's equivalent, 772 foot-pounds, the result will be the total heat of combustion expressed in foot-pounds. In the best coal this is as high as 12,000,000 foot-pounds. We arrive, therefore, at the conclusion that, to overcome the friction of the different parts of the machine; to whirl a mass of metal, weighing several hundredweights, round with a velocity of 1500 revolutions per minute; to generate a current of electric force far surpassing anything before produced; and, after allowing for the waste inherent in its passage through the conducting wires and electric lamp, to cause it to blaze forth with an intensity of light paling the rays of the sun; to keep up this intense development of energy for one hour—requires an expenditure of force represented by the combustion of less than 18½ ozs. of coal. This is the theoretical calculation; but if reduced to actual practice, the results are scarcely less astonishing. The *efficiency* of an engine, *i.e.* the ratio of the work actually performed to the mechanical equivalent of the heat expended, varies in extreme cases between the limits 0·02 and 0·2. Taking an average efficiency as 0·1, or one-tenth, we find that the ordinary consumption of coal required to work a 7 horse-power engine, midway between excessive wastefulness on the one hand, and rigid economy on the other, is 10 × 18½ ounces, or 11½ lbs. of coal per hour, worth about one halfpenny. This is, of course, only one item in the cost—to it must be added the expense of carbon rods for the lamp, which will be about ten inches per hour, worth perhaps a penny; there must also be added interest of the cost of purchase of machines, expense of maintenance and repairs, which will perhaps bring up the total expense per hour to sixpence or eightpence. Comparing this with the hourly expense of the electric lights already in existence, we find, according to the Abbé Moigno, that the French machine costs altogether sixpence per hour for a light equal to 900 wax candles; whilst the actual working expenses of maintaining the electric light at Cape La Hève, during a period of twenty-seven months have been, exclusive of salaries, about one shilling per hour, or inclusive of salaries, two shillings. According to a calculation made by the Abbé Moigno respecting the economy of the light evolved by the French machines, it appears that to maintain a light equal to 4000 wax candles for one hour would cost—with gas, £1 2s. 6d.; with colza oil, £1 7s.; and with the electricity produced by a Bunsen's pile, £1 15s. 6d. The annual expenditure at a first-class lighthouse on the old system is, on an average, £400 per annum; and on the assumption that the light burns for 4000 hours per annum, that would come to two shillings per hour. The expenses of the old and the electric system are therefore not very dissimilar; and the problem of the adoption of electricity to supersede oil must be decided on grounds of convenience and efficiency alone.

One cause of inconstancy in the electric lamp which hinders the adaptation to the purposes of lighthouse illumination is the unequal consumption of the carbon points. From experiments recently conducted for the Trinity House, Mr. Stevenson finds that the employment of a modified form of vacuum-tube removes this objection. The subject upon which we cannot enter more fully here is very exhaustively treated in Mr. Stevenson's recent work on the illumination of lighthouses.

The following Table exhibits the comparative illuminating power of the principal artificial lights:—

	a. Light-producing Substance.	β. Consumption per hour in grms.	γ Intensity of light. (1 wax candle = 100).	δ. Light obtained from 10 grms. of this material.	ε. Illuminating power (wax candles = 100).
	Wax	9·02	102·00	111·02	100
	Stearic acid	9·94	95·50	96·03	84
	Spermaceti	8·87	108·30	123·17	108
	Tallow	8·87	90·25	101·70	90
	Paraffin (1st quality)	8·83	—	94·69	83
	„ (2nd „)	8·49	—	139·87	123
Colza oil	Moderator lamp	40·69	694·00	170·07	159
	Kitchen lamp	7·33	45·67	62·30	55
	Reading lamp, without glass chimney	9·86	114·01	115·80	102
	Photogen	20·02	—	149·03	131
	Solar oil	26·82	—	225·64	199
	Petroleum	15·06	—	174·40	180
	„	8·09	—	186·01	195

According to Dr. Frankland's researches, the following quantities of illuminating materials exhibit equal illuminating power:—

Young's paraffin oil from Boghead coal	4·53 litres.
American petroleum (No. 1)	5·70 „
„ „ (No. 2)	5·88 „
Paraffin candles	8·42 kilos.
Spermaceti candles	10·37 „
Wax „	11·95 ,
Stearine „	12·50 „
Tallow „	16·30 „

Paraffin and Solar or Petroleum Oils.

Paraffin Oils. Paraffin was discovered in the year 1830 by Karl von Reichenbach among the products of the dry distillation of beech-wood tar, and has obtained its name from *parum*, little, and *affinis*, related to, on account of its incapability of chemically uniting with other substances. Paraffin is not acted upon by alkalies or acids, nor is it decomposed at a red-heat. It was afterwards found that paraffin is also formed by the dry distillation of peat, brown coal, Boghead, and some cannel coals, but not by the dry distillation of real coal. Paraffin is found native and occurs in large quantities in:—1. Petroleum, Rangoon and Persian, which sometimes contains 6 to 40 per cent. 2. In impure state, under the names of ozokerite, neft-gil, or mineral wax. 3. In bitumen, asphalte as contained in some schistose rocks, and as met with at Trinidad and elsewhere.

Manufacture of Paraffin. The mode of obtaining this substance differs according to its being an educt or a product. It is an educt as obtained from petroleum, ozokerit, neft-gil; but a product of the dry distillation of brown coal, peat, and the Boghead shale.

Preparation of Paraffin from Petroleum.

1. That petroleum contains paraffin was known in the year 1820, when A. Buchner discovered in the earth oil of the Tegernsee, in Upper Bavaria, a solid, fatty substance, which was afterwards ascertained by V. Kobell to be paraffin. Hence Buchner is locally considered to be the discoverer of paraffin; while later researches have proved that the earth oil of Baku, on the Caspian Sea; of Amiano, near Parma; and of Gabian, Hérault, France; contain this substance to greater or less extent. The idea of using these oils for the industrial preparation of paraffin dates only from 1856, when some samples of petroleum which were found to contain a large quantity of paraffin were imported into Europe. The American petroleums contain only a very small quantity of paraffin; but in those derived from Burmah and Rangoon, Gregory, De la Rue, and H. Müller found 10 per cent. Bleekrode investigated a sample of Java petroleum which contained 40 per cent of paraffin. The mountain naphtha of Eastern Galicia is with great advantage employed for preparing paraffin. According to Jacinsky, 45,000 cwts. of this material were in 1866 obtained from this naphtha.

The Rangoon oil obtained from Burmah as a native product flowing from springs in the neighbourhood of the river Irawadi is, according to De la Rue's patent (1854), treated in the following manner for the purpose of preparing paraffin and hydrocarbon oils. The crude oil is first put into a still, which can be heated by fire externally while steam is admitted internally. By this operation about 25 per cent of a fluid is obtained, which on being submitted to fractional distillation yields hydrocarbon, the sp. gr. of which varies from 0·62 to 0·86, while the boiling-point varies from 26·7° to 200°. The lightest and most volatile of these hydrocarbons is used as an anæsthetic, under the name of *Sherwood oil*, while the heavier oils are burnt in paraffin lamps. The residue of this first distillation—about 75 per cent of the original quantity—is again distilled, but with steam at 150° to 200°; and the products of variable volatility are separately collected. The last portions of the distillate contain chiefly paraffin, which is in crude state separated from the liquid by the application of artificial cold. The heavy oil is used as lubricating oil, and the paraffin is purified as already described.

Paraffin from Ozokerite and Neft-gil.

Paraffin is prepared from ozokerite and neft-gil, on the island Swätoi-Ostrow, in the Caspian Sea, about a verst (= 1066·78 metres) from the peninsula Apscheron, on the Caucasian shore. The neft-gil is carried by ships from Truchmenia. Paraffin is largely manufactured in Galicia from the mineral wax which occurs near Drohobicz and Boryslaw, also on the northern slopes of the Carpathian mountains, and in other parts of the Austrian Empire. The chief works are found at Aussig, Florisdorf, Ostrau, Vienna, New Pesth, Temisvar, &c. Mineral wax is also largely found in Texas.

Neft-gil, according to F. Rossmässller, is treated in the following manner:—15 cwts. of the crude material is put into iron stills provided with a leaden worm, and submitted to fractional distillation, yielding 68 per cent of distillate, consisting of 8 per cent of oil and 60 per cent of crude paraffin. The oil thus obtained is yellow, opalescent, possesses an ethereal odour, and a sp. gr. of 0·75 to 0·81. Each distillation yields a quantity of a light oil boiling below 100°, which is used for the purpose of purifying the paraffin. The crude paraffin obtained by the first distillation is tolerably pure, has a yellow colour, and can at once be treated by the hydraulic press and centrifugal machine. The oil from these operations is again submitted to fractional distillation in order to obtain more paraffin. The pressed paraffin is molten and treated at 170° to 180° with sulphuric acid, which is next neutralised by means of lime, and the paraffin again rapidly distilled; then again submitted to strong pressure, and the material obtained treated with 25 per cent of the light oil; then again molten, again pressed, and finally treated with steam for the purpose of eliminating the last traces of essential oil. The material obtained by this treatment is a perfectly pure, colourless material, free from smell, transparent, and so hard as to exhibit in large blocks an almost metallic sound. The fusion-point is 63° Rossmässler states that the raw material yielded to him in a week's time, after a previous continued distillation of two months, 148½ cwts. of paraffin ready for second pressure. The Galician ozokerite yields by distillation only 24 per cent of paraffin, and 45 per cent of paraffin oil, also termed ozokerite oil.

Paraffin from Bitumen. *c.* Paraffin is made in England from bitumen, asphalte, mineral tar, and the bituminous organic matter present in certain shales; among these, the so-called Kimmeridge clay, Boghead coal, and a few cannel coals. The asphalte occurring in Trinidad, Cuba, Nicaragua, Peru, California, and other countries, is used for the purpose of preparing paraffin and paraffin oils. The Cuba and Trinidad asphaltes yield 1·75 per cent paraffin. The extensive deposits of bituminous shale in Hungary are treated for paraffin and oil at Oravicza. According to Wünschmann, the shale yields 5 to 6 per cent of paraffin, 49 per cent of oil suited for burning in lamps, and 6 per cent of lubricating oil.

Preparation of Paraffin by Dry Distillation. The preparation of paraffin by the dry distillation of peat, brown-coal, coal-shale, Boghead coal, &c., involves two operations:—1. The preparation of tar. 2. The application of the latter to the preparation of paraffin oil and paraffin. The coal-tar of the gas-works does not contain paraffin, but naphthaline and anthracen.

Preparation of the Tar. 1. This operation is one of the most important and difficult of the industry, and during the last fifty years many enterprises undertaken for the application of fossil fuel to the preparation of illuminating materials have failed solely on account of the imperfect preparation of the tar. The making of the tar is carried on in retorts or in peculiarly constructed ovens, the distillation being in many cases assisted by the application of superheated steam. The principle of the construction of the tar oven is very simple, being that by a portion of fuel burning in the lower part of the oven, a layer, more or less thick, of superincumbent fuel, is submitted to a slow carbonisation, resulting in the production of tar, which flows downwards, while the gaseous products are lost. In order to prevent its violent combustion, the fuel is covered with a layer of clay. But as experience has shown that this mode of distillation is not well suited for the production of tar intended to yield paraffin and the oils, it is not general in practice on the large scale. although it has the advantage of being a continuous and uninterrupted process. According to report, an oven constructed by L. Unger, the manager of a paraffin works at Döllnitz, near Halle, yields suitable products, while a saving is effected in labour as well as in the quantity of fuel required for the distillation.

Horizontal retorts are frequently used for the preparation of tar, but experience has taught that if in the construction of the furnaces containing the retorts the arrangement is similar to that of a gas-works where four to eight retorts are worked in one furnace, no satisfactory results can be obtained, one of the reasons being that the principles of gas- and of tar-making are entirely opposed. It appears to be necessary to construct a furnace for every retort, and that the furnace should be of such dimensions as to be suited to hold a retort 10 feet long, 30 inches wide, and 15 inches high, forming in section a shallow oval. More recently there have been built in Bohemia and elsewhere brickwork retorts, shaped somewhat like a baker's oven. These seem to answer well, but are difficult to repair although of small first cost. Vohl observed that a quantity of 20 to 25 per cent of water present in the fossil material very greatly assists the formation and increases the yield of tar, owing to the superheated steam formed from the water during the distillation carrying off the vapours of the tar rapidly from the hot retort. This has given rise to the construction of Lavender's tar-producing apparatus, the principle of which is the same as that of Violetti's wood-charring apparatus used for the preparation of the charcoal in gunpowder manufacture. Lavender's apparatus consists of an iron cylinder provided with holes at the bottom for the purpose of admitting superheated steam, while to the top of the cylinder a tube is fitted for carrying off the products of the distillation. It would appear that L. Ramdohr's method of preparing tar from brown-coal by means of steam yields a tar which contains 22 to 24 per cent of paraffin and 36 to 38 per cent of oil.

Condensation of the Vapours of the Tar.

The condensation of the products of the dry distillation is one of the most important operations, and greatly influences the yield of tar. Vohl has lately proved that even when the construction of the retorts is not of the best, an average yield of tar may be obtained by attention to the condensation of the vapours. The complete condensation of the vapours of the tar is one of the most difficult problems the paraffin and mineral oil manufacturer has to deal with, while the means usually adopted for condensation, such as large condensing surfaces, injection of cold water, and the like, have proved ineffectual. It has often been attempted to condense the vapours of tar in the same manner as those of alcohol, but there exist essential differences between the distillation of fluids and dry distillation. In the former case the vapours soon expel all the air completely from the still and from the condenser, and provided, therefore, that—in reference to the size of the still and bulk of the boiling liquid—the latter be large and cool enough, every particle of vapour must come into contact with the condensing surfaces. In the process of dry distillation the case is entirely different, because with the vapours, say of tar, permanent gases are always generated. On coming into contact with the condensing surfaces, a portion of the vapours are liquefied, leaving a layer of gas as a coating, as it were, on the condensing surface. The gas being a bad conductor of heat, prevents to such an extent the further action of the condensing apparatus, that a large proportion of the vapours are carried on and may be altogether lost. A sufficient condensation of the vapours of tar can be obtained only by bringing all the particles of matter which are carried off from the retorts into contact with the condensing surface, which need neither be very large nor exceedingly cold, because the latent heat of the vapours of tar is small, and consequently a moderately low temperature will be sufficient to condense these vapours to the liquid state. The mixture of gases and vapours may be compared to an emulsion, such as milk, and as the particles of butter may be separated from milk by churning, so the separation of the vapours of tar from the gases can be greatly assisted by the use of exhausters acting in the manner of blowing fans. It is of the utmost importance in condensing the vapours of tar that the molecules of the vapours be kept in continuous motion, and thus made to touch the sides of the condenser. The condenser should not be constructed so that the vapours and gases can flow uninterruptedly in one and the same direction. The temperature at which the distillation is conducted greatly influences the yield of tar, and consequently of the paraffin and oil. As regards the influence of the shape of the retorts and mode of distillation, H. Vohl made the undermentioned comparative researches by distilling French and Scotch peat in horizontal retorts (No. I.), in vertical retorts (No. II.), and in ovens somewhat like coke-ovens (No. III.)

100 parts of peat yield of tar,—

	I.	II.	III.
French peat	5·59	4·67	2·69
Scotch peat	9·08	6·39	4·16

The sp. gr. of the tar from the different kinds of apparatus was as follows:—

	I.	II.	III.
French peat	0·920	0·970	1·006
Scotch peat	0·935	0·970	1·037

It appears from these results that horizontal retorts yield the largest, and ovens the smallest, quantity of tar; moreover, the duration of the operation of distilling is shortest in horizontal retorts, which also yield less gas, while in the ovens both tar and coke are burnt away to a considerable extent by the too great supply of oxygen.

Properties of Tar. The tar obtained from the retorts in distilling peat, brown-coal, lignite, bituminous shales, Boghead coal, &c., at as low a temperature as possible, and hardly higher than dull red-heat even towards the end of the operation, exhibits a coffee-brown colour, generally an alkaline, in some instances an acid, reaction, and possesses the very penetrating odour characteristic of tar. By exposure to air the colour of the tar becomes deeper, and sometimes even brownish-black. This tar often semi-solidifies at a temperature of 9° to 6°, owing to the paraffin it contains. The sp. gr. varies from 0·85 to 0·93, and consequently the tar floats on water. The so-called steam-tar, obtained by the aid of superheated steam from brown-coal (according to Ramdohr's plan, 1869) always has an acid reaction, and is completely saponified by alkalies; this tar becomes solid at a temperature of 55° to 60°, and can therefore be preserved in solid blocks in summer time. Its sp. gr. is 0·875.

As regards the quantity of tar obtained from 100 parts of raw material, the following results are most general:—

		Tar.	Sp. gr.	Crude paraffin. Per cent.
Foliated bituminous shale,	Siebengebirge	20·00	0·880	0·750
„ „	Hesse	25·00	0·880	1·000
Brown-coal,	Prussian Saxony	7·00	0·910	0·500
„	„	10·00	0·920	0·750
„	„	6·00	0·915	0·500
„	„	5·00	0·910	0·250
„	Bohemia	11·00	0·860	—
„	Westerwald	5·50	0·910	—
„	„	3·50	0·910	—
„	Nassau	4·00	0·910	—
„	„	3·00	0·910	—
„	Frankfort	9·00	0·890	—
Lignite,	Silesia	3·00	0·890	0·25
Shale,	Vendée	14·00	0·870	1·000

		Tar.	Sp. gr.	Crude paraffin. Per cent.
Shale,	Westphalia	5·00	0·920	0·050
Schist,	Würtemburg	9·63	0·975	0·124
Peat,	Neumark	5·00	0·910	0·330
"	Hanover	9·00	0·920	0·330
"	Erzgebirge	5·70	0·902	0·350
"	"	5·30	0·905	0·400
"	Russia	5·86	—	—
"	"	7·00	—	—
Boghead coal,	Scotland	33·00	0·860	1—1·4
Cannel coal,	"	—	—	1—1·3
Peltonian coal,	"	—	—	1·000
Coarse coal,	"	9·00	0·910	1—1·25

Mode of Operating with the Tar. The first thing to be done with the crude tar is to separate the water, which is effected by pumping the tar into the dehydrating apparatus. These apparatus consist of tanks of boiler-plate, placed within a larger tank, so that a space of 10 centims. intervenes, into which water is poured and maintained by means of steam at a temperature of 60° to 80° for ten hours. After this time the ammoniacal water and other impurities, together about one-third of the bulk of the crude tar, have become separated, while the small quantity of water still adhering to the tar is of no consequence in the further operations. The tar is decanted by opening a stop-cock or valve placed near the top of the tank, and the ammoniacal water is removed by opening a stop-cock at the bottom.

Specifically light tars are of course readily separated from the water, while heavy tars are more difficult to deal with. If to the ammoniacal water of such tars salts are added, for instance, common salt, Glauber salt, chloride of calcium, and the like, the specific gravity of the water is increased, and the heavy tar more readily separated; but according to Dullo these means are either too expensive or do not quite answer the purpose. The complete separation of the tar from the water is of the greatest importance, because in the subsequent distillation the presence of water may cause the tar to boil over and give rise to serious accidents by coming in contact with the fire under the stills.

Distillation of the Tar. This operation is usually carried on in cast-iron stills large enough to hold 20 cwts. of tar. In order to prevent the flame impinging on the bottom of the still, it is protected by a fire-brick arch. The still is usually built in two separate parts, which are joined with a flange and bolts, so that if the lower part is burnt out, only that requires to be renewed.

The helms of these stills are rather flat and the spout very wide. The vapours of the various oils have a high density and low latent heat, so that these vapours have a tendency to condense readily and flow back into the still; therefore the helm is covered with sand or ash, being bad conductors of heat. When the tar is thoroughly dehydrated, the distillation proceeds quietly and without ebullition; but if any water be mixed with or adheres to the tar, the liquid in the still boils violently and is very apt to boil over. At below 100° the tar loses the very volatile sulphide of ammonium and the pyrrhol bases, while gases are evolved which ought to be allowed to escape by a safety-valve. The true distillation begins at 100°, yielding at first a distillate consisting of very strong ammoniacal liquor and some light oils. The boiling-point of the tar is not constant, the oil coming over uninterruptedly when the temperature has risen to above 200°; then the boiling-point becomes somewhat constant, while with the oil some water comes over, due to the chemically-combined water of the carbolic acid being set free. The distillation then again becomes somewhat interrupted, and can be maintained only by stronger firing of the retort. The oils now distilling over become solid on cooling, owing to the large proportion of paraffin they contain. The distillation is continued to dryness, the asphalte left in the still being removed after about four or five operations, and for this purpose the still is somewhat cooled and the molten asphalte run off by a tap at the bottom of the still. If the distillation is carried to dryness, some water finally distils over, due to the decomposition of the organic matter. A still of 500 litres capacity can be distilled off in twelve to fourteen hours, if the operation is pushed so far as to decompose the asphalte, leaving only a carbonaceous residue; but if the asphalte is to be collected, the distillation must be stopped after eight to ten hours. The still is separated from the condensing apparatus by a massive wall, through which the spout of the helm is passed into the leaden worm serving as a condenser, and kept cool by being placed in a wooden tank filled with cold water. But as soon as the paraffin magma begins to come over the water is allowed to become warm, in order to prevent the paraffin solidifying in the worm. The gases which are evolved towards the end of the distillation are carried off by a pipe communicating with the chimney.

Treatment of the Products of Distillation. The mixed products or raw oils obtained by the distillation are poured into a large cast-iron cylinder and mixed with a solution of caustic soda so as to cause the latter to act upon, and intimately combine with, the acid substances (homologues of carbolic acid)—simply termed creosote in the works—and pyroligneous acid—which impart an offensive odour and dark colour to the oils. When the mixture of the oils and caustic soda solution has been effected, the fluid is run into an iron tank and allowed to settle; the creosote-soda is then removed, and the oil washed with water to eliminate any adhering alkali. The crude oil is next similarly treated with sulphuric acid for the purpose of removing basic substances, which impart odour and colour. The quantity of acid to be used and the duration of its action, aided sometimes by heat, depend upon the nature of the crude oil—5 per cent of acid of 1·70 sp. gr. and five minutes action are sometimes sufficient, while in other cases 25 per cent of acid will be required, and three hours' contact with the oil. The action of the sulphuric acid should be carefully watched, as it may injure the quality of the oil by decomposing some of the lighter hydrocarbons, whereby sulphurous acid is given off. The mixture of acid and oil is allowed to settle; the former is run off, and the latter washed first with water then with very dilute soda ley, and is finally poured into the rectifying stills. The solution of creosote-soda is neutralised with the sulphuric acid from the preceding operation, the result being that crude carbolic acid is obtained, which is used for various purposes; such as impregnating wooden railway sleepers, as a disinfecting material, or for preparing certain tar-colours (see p. 580). More recently the creosote-soda has been used for gas manufacture, leaving a coke containing soda, the soda being abstracted by lixiviation with water.

Rectification of the Crude Oils. This operation is conducted precisely as the distillation of the tar. The oils are separated according to their greater or less volatility and specific gravity, or are kept mixed, as paraffin oil, at a sp. gr. of 0·833, and sent as such to the market. When the oil which comes over begins to solidify on cooling or exhibits a sp. gr. of 0·88 to 0·9, it is separately collected and placed in a cool situation for the purpose of crystallising the paraffin. The vessels in which the paraffin magma is placed for the purpose of solidifying are rectangular iron tanks, fitted with a tap, or are conical, sugar-loaf shaped vessels, made of iron or wood, and from 1·6 to 2 metres high, and 1 metre wide at the top, being provided with a tap for the purpose of removing the oily matter which has not solidified after the lapse of about two to four weeks. This thick oil is next cooled to far below the freezing-point of water, in order to obtain more paraffin and other hydrocarbons mixed with it. Any still non-solidified matter is, when it has a low specific gravity, again refined by distillation, and will yield paraffin oil; but if its sp. gr. is high—say from 0·925 to 0·940—it is used as a lubricating oil, known abroad as Belgian waggon grease.

Refining of the Crude Paraffin.

The crude paraffin is in England sold to the refiners, who are also paraffin-candle makers; but on the Continent every manufacturer of crude paraffin refines his product and converts it into candles. The crude paraffin, so-called paraffin butter, is treated in various ways: some manufacturers crystallise it by the aid of cold, and press it for the purpose of removing any oil; others again first treat the crude material with caustic alkali ley, next with sulphuric acid, and then again distil it or leave it to crystallise. The caustic soda ley removes from the paraffin all the acid substances and other impurities it may contain. The partly purified paraffin is now treated with 6 to 10 per cent of sulphuric acid, whereby alkaline and resinous matters are removed. The loss in bulk of the crude material by these operations amounts to about 5 per cent. The purified paraffin is next allowed to remain in a very cool place for some three or four weeks; after which the nearly solid mass is filtered, then submitted to the action of centrifugal machines, and finally strongly pressed. The oil which is separated from the paraffin is again distilled, yielding paraffin oil and paraffin butter. The solid paraffin is molten, cast into blocks, and these submitted to very powerful hydraulic pressure. The pressed cake is next treated at 180° with 10 per cent of sulphuric acid for two hours, then washed with hot water, again cast into blocks, again pressed, and then washed with a solution of caustic soda. Instead of treating the paraffin with active agents, it has been proposed to use neutral solvents for the removal of the oily materials; for this purpose, benzol, light tar oils, benzoline, and sulphide of carbon, have been employed in the following manner:—The crude paraffin is first hot-pressed, and the pressed mass fused with 5 to 6 per cent of the solvent; having been again cast into blocks, these are pressed, and the operation repeated if necessary. The paraffin having thus been made quite white and pure, is again fused and treated with high-pressure steam, forced into the molten mass for the purpose of volatilising the last traces of the solvents. The sulphide of carbon, first employed by Alcan (1858) for refining paraffin, is used in the following manner:—The paraffin is melted at the lowest possible temperature, then well mixed with 10 to 15 per cent of sulphide of carbon, after which the cooled and solidified mass is strongly pressed, the expressed fluid being submitted to distillation for the purpose of recovering the sulphide of carbon. The paraffin is next fused and kept in liquid state for some time for the purpose of eliminating the adhering sulphide of carbon.

Hübner's Method of Preparing Paraffin.

Instead of following the preceding method with the crude tar, Hübner treats it first with sulphuric acid, and next distils the tar, separated from the acid, over quick-lime. The crude paraffin obtained is pressed, and then further refined by treating it with colourless brown-coal tar oil. The advantages of this method—by which *one* distillation is saved—are:—

a. A larger yield of paraffin.

β. A material of better quality and greater hardness than by the usual method.

With the paraffin the so-called paraffin oils are obtained; but this industry has been greatly crippled by the extensive importation of paraffin oils (really petroleum oils) from America, so that the aim of the paraffin makers is to increase the yield of paraffin. By Hübner's method of distillation over quick-lime, 40 to 50 per cent of impurities (chiefly empyreumatic resins and creosote) are removed, which by the old process are only got rid of at greater expense by the use of caustic soda.

Yield of Paraffin. As regards the yield of paraffin, paraffin oil, and lubricating oil, from the various kinds of raw materials, we quote the following particulars. At the Bernuthsfeld works, near Aurich, the excellent peat yields 6 to 8 per cent of tar; 20 per cent of paraffin oil, of sp. gr. = 0·830; and 0·75 per cent of paraffin. H. Vohl obtained from 100 parts of peat-tar from the peat of undermentioned localities:—

	Paraffin Oil. Sp. gr., 0·820.	Lubricating Oil. Sp. gr., 0·860.	Paraffin.
Celle (Hanover)	34·60	36·00	8·01
Coburg	20·62	26·57	3·12
Damme (Westphalia) ...	19·45	19·54	3·31
Zurich (Switzerland) ...	14·40	8·66	0·42
Russia	20·39	20·39	3·36
Westphalia	11·00	19·48	2·25

Brown-Coal. In the works situated in the Weissenfels brown-coal mineral district, 1 ton (= 275 to 300 lbs.) of the mineral yields 35 to 50 lbs. of tar. 100 lbs. of this tar yield 8 to 10 lbs. of hard paraffin suited for candle-making, and further 8 to 10 lbs. of soft paraffin for use in stearine-candle making, as well as 43 lbs. of paraffin oil. Hübner's works at Rehmsdorf, near Zeitz, yield annually from 360,000 cwts. of brown-coal about 40,000 cwts. of tar, yielding 18,000 cwts. of crude oil, 4000 cwts. of refined paraffin oil, and 6000 cwts. of paraffin.

100 parts of retort-tar (in contradistinction to steam-tar) from brown-coal yield:—

Brown-coal from—	Paraffin oil. Sp. gr., 0·820.	Lubricating oil. Sp. gr., 0·860.	Paraffin.	
Aschersleben, Prussia	33·50	40·00	3·3	Analysed by Vohl.
Frankenhausen „	33·41	40·06	6·7	
Münden „	17·50	26·21	5·0	
Oldisleben „	17·72	26·60	4·4	
Cassel „	16·42	27·14	4·2	
Der Rhön, Bavaria	10·62	19·37	1·2	
Tilleda, Prussia ...	16·66	18·05	4·4	
Stöckheim, near Düren „ ...	17·50	26·63	3·2	
Bensberg, near Cologne „ ...	16·36	19·53	3·4	
Tscheitch, Austro-Hungary ...	9·04	28·86	3·2	Analysed by C. Müller.
Eger „ ...	9·14	54·00	5·2	
Herwitz „ ...	22·00	48·32	5·2	
Schöbritz „ ...	21·68	46·33	4·3	

Ramdohr obtained (1869) from steam-tar from brown-coal on an average—

$$22 \text{ to } 24 \text{ per cent paraffin} \begin{cases} 15 \text{ per cent fusing at } 56 \text{ to } 58^\circ \\ 7 \text{ to } 9 \quad ,, \quad ,, \quad 38^\circ \text{ to } 47^\circ \end{cases} \text{and}$$

36 to 38 per cent of oil.

With careful management steam-tar may yield 28 to 30 per cent paraffin.

The quotations of the yield from cannel and Boghead coals vary very much. 100 parts of tar from bituminous shale were found to yield:—

	Mineral oil.	Lubricating oil.	Paraffin.
English bituminous shale	24·28	40·00	0·12
Bituminous shale from Romerickberg, Prussia	25·68	43·00	0·11
„ „ Westphalia „	27·50	13·67	1·11
„ „ Oedingen on the Rhine „	18·33	38·33	5·00

According to Müller (1867), 100 parts of Galician mineral wax (ozokerite) yield 24 per cent of paraffin and 40 per cent of oil.

Properties of Paraffin. Pure paraffin is a white, wax-like, tasteless, and inodorous substance, with a slightly fatty appearance. Its sp. gr. is 0·877. It is harder than tallow, but softer than wax. Its properties vary, however, according to the raw materials from which it has been obtained. Paraffin from Boghead coal has been obtained, after melting, in a very crystalline state, and with a fusion-point at 45·5°; while, again, it has been obtained granular as bleached wax, with a fusion-point of 52°. Paraffin from Rangoon oil was found to fuse at 61°, and that from peat at 46·7°. The paraffin from the tar of Saxony brown-coals fuses at 56°, and the oil paraffin at 43°. The native paraffin from ozokerite fuses at 65·5°. The composition of the various kinds of paraffin is:—

	From Saxony Brown-coal.	From Ozokerite.	From Boghead mineral.	From Peat.	From Petroleum.
Carbon ...	85·02	85·26	85·00	84·95—85·23	85·15
Hydrogen .	14·98	14·74	15·36	15·05—15·16	15·29

From these figures the conclusion may be drawn, contrary to the view generally adopted, according to which all varieties of paraffin should be mixtures of hydrocarbons constituted as C_nH_n (whether the paraffin be obtained from brown-coal, peat, ozokerite, or petroleum), that paraffin is a mixture of hydrocarbons homologous with marsh-gas, many of which contain no less than C_{27}. Paraffin is insoluble in water, but soluble to some extent in boiling alcohol; 100 parts, however, dissolve when boiling only 3 parts of paraffin. Paraffin is soluble in ether, oil of turpentine, oil of olives, benzol, chloroform, and sulphide of carbon. Paraffin boils above 300°, and may be distilled without undergoing any alteration. Acids, alkalies, and chlorine do not at all act upon paraffin at the ordinary temperature; but when chlorine is caused to pass into molten paraffin, hydrochloric acid is evolved and chlorinated products formed. Paraffin may be fused with stearine, palmitine, and resins in all proportions. Paraffin is used for making candles (see p. 630), but has been employed now and then as a lubricating material; also for preserving timber; for rendering wine and beer casks water-tight; for the purpose of preventing the foaming and boiling over of the sugar solutions in the vacuum pans at the beginning of the ebullition. It has been suggested to use paraffin for preserving meat; for waterproofing fabrics (Dr. Stenhouse's process); for use instead of wax for waxing paper (employed in pharmacy under the name of *charta cerata*); instead of stearic acid for soaking plaster-of-Paris objects. Finally, paraffin is used in the manufacture of the better varieties of matches, as a waterproof varnish for coating the phosphorus composition; and in chemical laboratories to replace oil in the oil-baths.

Paraffin oil. As already mentioned, the dry distillation of Boghead mineral, brown-coal, peat, and bituminous shales, yields tar, the quantity of which varies according to the nature of the raw material and other conditions, mode of distillation, degree of heat, &c. As regards the nature of tar we cannot say that it is fully elucidated. Until the year 1830, tar was considered to be simply a solution of empyreumatic resins, rich in carbon, in empyreumatic oil or oils, the nature of these substances being left undecided. The late Baron von Reichenbach was the first who seriously investigated the nature of tar, and the result was the discovery of paraffin and of eupion, a very volatile liquid, highly inflammable, and found to boil at 47° to 169°, consequently a mixture of various substances. Notwithstanding the high merits of Reichenbach's researches, the constitution of tar was not fully elucidated. In an industrial point of view tar has many important applications, especially for the preparation of illuminating materials; for by a rectifying and fractioned distillation, tar yields paraffin and paraffin oils, when the heavy oils and acids have been previously separated. Paraffin oils—met with in the trade under various names, such as solar oil, photogen oil, ligroine oil, &c.—are very similar to petroleum oils, and consist like them of carbon and hydrogen, and are, when thoroughly rectified, almost colourless and free from smell.

The mineral oils now met with in commerce are distinguished as:—Photogen, prepared in Saxony, and consisting of a mixture of oils boiling between 100° and 300°. It is a colourless, very mobile fluid, exhibiting a characteristic ethereal smell, and a sp. gr. of 0·800 to 0·810; but the sp. gr. of its constituent oils varies from 0·76 to 0·86. Formerly there were met with in the trade light photogens of a sp. gr. of 0·78, consisting chiefly of a so-called essence, of 0·72 sp. gr. and boiling below 60°; but this oil was found to be too inflammable, and is now used as benzoline (also known as naphtha, ligroine, Canada oil, &c.) in the sponge-lamps, and for other purposes. Solar oil, or German petroleum, is a colourless or faintly yellow-coloured fluid of about the same consistency as colza oil, and of a sp. gr. of 0·830 to 0·832. The boiling-point lies between 255° and 350°; cooled to −10° it should not deposit paraffin, while its vapour is not inflammable below 100°. Pyrogen is a kind of paraffin oil invented by Breitenlohner and prepared from residues of crude oils which contain carbolic acid, paraffin, and other substances, and exhibit a sp. gr. of 0·895 to 0·945; these materials, which accumulate in tar-works, are converted into pyrogen by a process presently to be described, yielding a light straw-yellow oil of 0·825 to 0·845 sp. gr. Engine-oil, or lubricating oil, also known as Vulcan oil, is a thickly fluid oil imported in large quantities from the United States, and which deposits, when submitted to cold, a large quantity of crystals of paraffin. This oil is obtained largely in the paraffin oil and petroleum-refining works. According to A. Ott's account, the American lubricating oil is not obtained by distillation, but simply by defecating a specifically heavy native petroleum with charcoal so as to eliminate the colour. This lubricating oil is sometimes mixed with a certain percentage of vegetable or animal fats. The oil is largely used for lubricating cotton-spinning machinery, but notwithstanding its extensive employment, the production far exceeds the consumption; it should be as much as possible re-converted into paraffin oil and pyrogen. In America and on the Continent a large quantity is employed for making gas.

Preparation of Mineral Oil.

The manufacture of these oils is a collateral industry with the manufacture of paraffin. The products of the distillation of tar are first treated with a solution of caustic soda. This operation aims at the removal of carbolic and acetic (pyroligneous) acid compounds, which impart to the oil a disagreeable odour and dark colour. The quantity of soda to be used may vary from 5 to 6 or even 20 per cent, and the operation requires, in some instances, the aid of heat for about two hours, while in others, again, the end is attained in two minutes and at the ordinary temperature of the atmosphere. The mixture of soda ley and other substances is then run into a large tank for the purpose of depositing the soda ley and combined compounds, which, when settled, are run off, and the oil washed with water until it has become free from alkali. The oil is next treated with sulphuric acid of 1·7 sp. gr., the quantity of which may vary from 5 to 25 per cent, while the duration of the operation may vary from one minute to three hours. The treatment with sulphuric acid greatly influences the quality of the oil, because it might happen that, by this treatment, oils originally free from sulphur would become impregnated therewith, in consequence of the fact that the more volatile portions of these oils are essentially mixtures of aldehydes and ketones, bodies which readily combine with sulphurous acid. The mixture of oil and sulphuric acid is run into a tank for the purpose of depositing the specifically heavier portions of the liquid; the supernatant lighter oil is afterwards tapped off, and washed with plenty of water, then with weak caustic soda ley, being finally rectified by distillation. According to H. Vohl, paraffin oils are sometimes bleached with hydrofluoric acid, whereby fluorine compounds are stated to be formed, which, on burning the oil, give off noxious vapours. The alkaline and acid liquors used in the operation are utilised in the following manner:—The crude alkaline carbolic acid liquor is saturated with sulphuric acid, and crude carbolic acid obtained. The latter is used for various purposes, among which are the creosoting of timber, for disinfecting, &c.; or it is used for preparing pyrogen by causing the vapours to pass through a red-hot tube, the condensing product being, after treatment with soda ley and sulphuric acid, as well fitted for burning in lamps as paraffin oil. Perutz submits the alkaline liquid containing carbolate of soda to distillation in an iron still, pushing the operation on to dryness, and obtaining a mixture of carbolic acid with light fluid hydrocarbons. If it is desired to prepare pure carbolic acid, the liquid which comes over between 140° and 240° is separately collected and treated in the ordinary manner. The residue left in the still, a mixture of alkalies and coke, is calcined, the ash lixiviated, and the resulting liquor causticised with lime. The sulphuric acid is employed for preparing sulphate of iron. The rectification of the oils is performed in the ordinary manner. 100 parts of peat tar yield of rectified products:—Sclar oil of 0·865 sp. gr., 26·4; photogen, 0·830 sp. gr., 20·7; paraffin, 23·3; crude carbolic acid (peat-tar creosote), 11·0 parts. 100 parts of Saxony brown-coal tar yield on an average:—Paraffin, 10 to 15 photogen, 16 to 27; solar oil, 34 to 38; creosote, 5 to 10; coke, 15 parts. The commercial value of these articles fluctuates and depends on the demand and supply. There were prepared in 1870 in Prussia from 5½ millions of cwts. of brown-coal in sixty-seven different works, 100,000 cwts. of paraffin and 250,000 cwts. of mineral or paraffin oil.

Petroleum.

Petroleum Oil, and its Occurrence. Since the year 1859 native petroleum has become a most important illuminating material. Petroleum was known to the ancients and was used by them for various purposes. Greece obtained it from the Island of Zante; and the petroleum from Agrigentum was burnt in lamps under the name of Sicilian oil. The inspissated oil which was used under the name of mineral-pitch, or asphalte, as a cement in building Babylon, was obtained from the neighbourhood of the River Euphrates. Mineral pitch was used by the ancients for embalming their dead, while it would appear that some black-coloured earthenware was prepared with asphalte gently burnt in. In some parts of Central Asia large quantities of inspissated petroleum occur, and the Dead Sea is especially a locality where this substance is met with; hence the name of *lacus asphaltites*. In the Island of Trinidad a large lake (Pitch Lake) occurs, filled with mineral pitch, which according to the prevailing temperature is more or less soft. Petroleum is found in a great many localities in different parts of the world—Amiano, near Parma, where this oil has been used for burning in street lamps; Tegernsee, Bavaria, the oil-spring having been known since 1430, but yielding only 42 litres annually; Neufchâtel, Switzerland; Sehnde, near Hanover; Kleinschöppenstedt, Brunswick; Bechelbronn, Alsace; Coalbrookdale, England; in the Pyrenees, and other portions of Spain and France; also in Galicia. In far larger quantity petroleum occurs on the Caspian seaboard at Apscheron, and especially on the Island of Tschellekan (39½° N. lat.), where more than 3400 sources are found, which yield annually 54,000 cwts. of petroleum. At Rangoon, in Burmah, petroleum occurs in such large quantity that annually 400,000 casks, weighing 6 cwts. each, are exported thence. But in no country is petroleum found in such inexhaustible quantity as in the United States, in a tract parallel to the Alleghany mountains, and extending from Lake Ontario into the Valley of the Kanawha, in Virginia. The oil region includes the western counties of the State of New York and Pennsylvania, and part of Ohio. The most important petroleum-wells are at Mecca (Trumhall Co., Ohio), and at Titusville, Oil City, Pithole City, Rouseville, McClintockville (Venungo Co., Pennsylvania, the country of the Seneca Indians). This territory is termed Oil Creek. The wells are bored to a depth of 22 to 23 feet: some wells are flowing wells, the oil being yielded spontaneously; other wells are pumped. In Canada petroleum is met with in different localities; as, for instance, at Gaspe, near the St. Lawrence, and in Lambton Co.; also on the western portion of the peninsula formed by the lakes Huron, Erie, and Ontario, in the Enniskillen district. California yields enormous quantities of petroleum, which occurs also in many parts of South America, and in the islands of Java, Borneo, and Timor.

Origin and Formation of Petroleum. As regards the origin and formation of petroleum, several hypotheses have been brought forward. According to some the formation of petroleum is intimately connected with the occurrence of hydrocarbons met with—according to the observations of Dumas, H. Rose, and Bunsen—in compressed condition in many rock-salt deposits, from which they are set free either in the state of gas or as naphtha, when the salt comes into contact with water or is broken up. The crackling salt of the Wieliczka mine gives off marsh-gas; but by condensation CH_4 might yield homologous hydrocarbons, C_6H_{14} and C_7H_{16}, which form the bulk of the volatile portions of petroleum and paraffin, the composition of the latter varying between

$C_{20}H_{42}$ and $C_{27}H_{56}$. The association of petroleum, rock-salt, and combustible gases is met with in a great many localities; as, for instance, in the Bavarian Alps, in Tuscany, Modena, Parma, the Carpathian mountains, on the Caspian Sea, in India, and also in America. According to another view, petroleum is the product of the slow decomposition of vegetable and animal matter, and results from a re-arrangement of their elements. The American geologists suppose petroleum to be due to the dry subterraneous distillation of accumulations of sea-plants and marine animals, and that the petroleum is forced upwards by water, always present in the bored wells. Of course the hypothesis involves the action of subterraneous heat at great depth, which, according to existing observations on the increase of temperature in deep coal mines, reaches the boiling temperature of water at 8000 feet. According to Berthelot's view (1866), there should be formed subterraneously, from carbonic acid and alkali metals, acetylides, which again should yield with aqueous vapour acetylen, C_2H_2, which in its turn should be converted into petroleum and tar products.

Refining of Crude Petroleum.

Almost all the native petroleums require to be refined before they can be used as illuminating material, the mode of refining differing according to the nature and consistency of the oil. The oils met with at Apscheron, in Russia, and in the neighbourhood of Baku, are nearly all colourless, and can be directly used for burning in lamps after having been simply rectified by distillation. The Rangoon oil contains so large a quantity of paraffin that it has at the ordinary temperature the consistency of butter, and is therefore employed for extracting paraffin. The native petroleums of many of the East Indian islands contain sulphur compounds, and cannot therefore be burnt in lamps until they have been treated with caustic soda and sulphuric acid, and rectified by distillation. The specific gravity of the native petroleums met with in Canada and the United States varies very much; that from Venungo Co., Pennsylvania, has a sp. gr. of 0·8, while oils in other localities have a sp. gr. of 0·85 to 0·9. Galicia produces large quantities of native petroleum, which is refined in some twenty-two works, situated near Boryslav and Drohobicz; while a large quantity of paraffin oil is obtained as a by-product of the distillation of paraffin from ozokerite. The lighter petroleums yield about 90 per cent of photogen and solar oil, but the heavier kinds yield only 40 to 50 per cent, the remainder being tar. The methods of refining native petroleums consist in treatment with caustic soda, sulphuric acid, and finally fractioned distillation.

Constitution of Petroleum.

As far as researches have been instituted, all the native petroleums, irrespective of consistency and specific gravity, are mixtures of the higher series of the homologous compounds, of which marsh-gas, CH_4, is the first term.* Amyl hydrogen, hydride of amyl, C_5H_{12}, boiling at 68°, and hydride of caproyl, C_6H_{14}, boiling at 92°, constitute the more volatile portion of crude American petroleum; these burn like marsh-gas with a faintly luminous flame. The constituents of the oil used in lamps are represented by the hydrocarbons C_7H_{16} and $C_{12}H_{26}$. The higher series of the marsh-gas group exhibit a butter-like consistency, and are composed according to the formulæ $C_{20}H_{42}$ and $C_{27}H_{56}$, and belong to the paraffins met with in petroleums.

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* Ronalds proved in 1865 that the gases evolved from crude American petroleum are essentially hydride of ethyl (C_2H_6), and hydride of propyl (C_3H_8), which are the second and third terms of the above series. The researches of Fouqué (1869) agree with those of Ronalds, for he found that the gases evolved from petroleum are partly a mixture of the hydrides of propyl and butyl, and partly a mixture of marsh-gas and hydride of ethyl.

Technology of Petroleum. According to an Act of Congress crude petroleum may not be exported, owing to its high degree of inflammability, and a sample of every cask of petroleum is to be tested. The oil ought not to give off inflammable vapours (hydride of butyl) below 38° C. = 100° F. In the United Kingdom, as elsewhere, legislative measures have been taken in order to insure safety in the petroleum trade. Consequently crude petroleum is chiefly refined by submitting it to fractional distillation in order to separate from it the naphtha of 0·715 sp. gr. (the benzoline of the shops), which begins to boil at 60°. Wiederhold found that the naphtha yields by fractional distillation:—

48·6	per cent of	0·70	sp. gr. boiling at	100°	(*a*)
45·7	,,	0·73	,, ,,	200°	(*b*)
5·7	,,	0·80	,, ,,	above 200°	(*c*)

(*c*) is refined petroleum; (*a*) is too volatile for burning in lamps; (*b*) may be used in properly constructed or sponge lamps. H. Vohl calls petroleum naphtha, canadol or Canada oil, and applies it to the carburetting of illuminating gas; and also as a solvent for caoutchouc, colophonium, mastic, dammar, copal, amber, shellac, oils and fats, and for preserving anatomical preparations. The most volatile and lightest portion of the naphtha (sp. gr. 0·65, boiling-point between 40° and 50°), known as *Sherwood oil*, keroselen, petroleum ether, and rhigolen, is used as an anæsthetic, and applied externally in neuralgia. The less fluid petroleum oils are used as lubricating oils under a variety of names—Globe oil, Vulcan oil, Phœnix oil, &c. Crude petroleum is used as fuel in the Russian navy, in steamers on Caspian Sea, and by the United States navy in some cases; it has been tried with success in France as fuel for locomotive engines. Refined petroleum, the paraffin oil of the London shops, is an opalescent fluid, somewhat yellow, boiling at 150°, not miscible with water, alcohol, and wood-spirit; but readily miscible with ether, oil of turpentine, and sulphide of carbon. Petroleum dissolves, especially when hot, asphalte, elemi, Venice turpentine, and caoutchouc. As is well known, petroleum is largely used for burning in lamps. The fluid known as kerosine, also used for burning in lamps, has a sp. gr. of 0·78 to 0·825. Pitt oil seems to be identical, and both are prepared from American petroleum by distillation. As a great confusion exists in the names of the various distillation products of petroleum, we quote the following particulars communicated by Kleinschmidt, of St. Louis:—

Oils distilling over below	37·7°	sp. gr.	0·60°	= 90°—97° B.	= Rhigolin.
,, at	76·6°	,,	0·63—0·61	= 80°—90° B.	= Gasolin.
,, ,,	137·0°	,,	0·67—0·63	= 70°—80° B.	= Naphtha.
,, ,,	148·0°	,,	0·73—0·67	= 60°—70° B.	= Benzine.
,, ,,	183°—219°	,,	0·78—0·82	= 40°—60° B.	= Kerosen.

At higher temperatures paraffin and illuminating gas come over. In order to give some idea of the enormous consumption of petroleum, it may be mentioned that the imports in the German Customs Union,* amounted in 1866 to 918,954 cwts., and in the first half-year of 1870 to 1,260,630 cwts.

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* Embraces all the States of Germany, including the Grand Duchy of Luxembourg, but no Austrian territory.

DIVISION VIII.

FUEL AND HEATING APPARATUS.

A. FUEL.

Fuel. We understand by fuel such combustible materials as may be burnt with the view of obtaining heat. Wood, peat, brown-coal, coal, anthracite, wood-charcoal, peat-charcoal, coke, petroleum, combustible gases, such as carbonic oxide and hydrocarbons, are fuel. Excepting the gases, all kinds of fuel are closely related to each other as far as regards their origin, because fuel consists of cellulose or has been formed from it. Native fuel, coal, wood, peat, anthracite, consists of carbon, hydrogen, and oxygen, with larger or smaller quantity of ash (silica, alumina, oxide of iron, alkalies, and alkaline earths), and as regards coals, also nitrogen, sulphur, and phosphorus. Only hydrogen and carbon are combustible substances, and these, therefore, determine the value of fuel by complete combustion, leaving only ash, water, and carbonic acid. In wood-ash, carbonate of lime, in the ash of mineral fuel, alumina, chiefly prevail. The effect of fuel depends upon :—

a. Combustibility.
b. Inflammability.
c. Calorific effect.

Combustibility. By combustibility is understood the greater or less readiness with which fuel is kindled and continues to burn after having been kindled. This property depends upon the composition of the fuel. A porous fuel kindles more readily than a denser and more compact fuel. With regard to the relation between combustibility and composition, it has been found that the more hydrogen a fuel contains, the more readily it burns.

Inflammability. By the inflammability of fuel we understand its property of bursting into flame when kindled; and as flame is due only to burning gases, it is evident that the fuel containing most hydrogen is that which burns with the most intense flame. In the case of coke, charcoal, and similar fuel, there can be no flame other than that due to the formation of carbonic oxide owing to incomplete combustion.

Calorific Effect. The heat evolved by the complete combustion of fuel may be measured in two different ways :—

1. As regards the quantity of heat evolved.
2. As regards the degree of temperature or intensity of the heat.

When the heat evolved is measured according to its quantity, we obtain the combustive power, the specific or absolute calorific effect, of the fuel.

When the degree of heat is measured, the heating power or pyrometrical effect of the fuel is ascertained. These two measurements together determine the technical value of a combustible material. When the absolute calorific effect of a fuel is referred to its cost, we determine its combustible value in the locality where it is to be consumed.

Determination of Combustive Power. As we do not possess a particular measure for heat, we have, when desirous of determining the quantity of heat yielded by a fuel, to institute trials for the purpose of ascertaining the relative quantity of heat evolved by various kinds of fuel, in order that by comparison we may find how much more heat is evolved by one kind of fuel than by another. If the results thus obtained are referred to a given bulk of the fuel experimented with, we obtain its specific calorific effect; but if it be referred to a given weight, we obtain the absolute heating effect. The following table exhibits the heat of combustion of several substances:—

Hydrogen	yields	34,462	units of heat.
Carbon (when completely burned and yielding carbonic acid)	,,	8080	,,
Carbon (when yielding carbonic oxide)	,,	2474	,,
Carbonic oxide	,,	2403	,,
Marsh-gas	,,	13,063	,,
Elayl-gas	,,	11,857	,,
Crude petroleum	,,	11,773	,,
Ether	,,	9027	,,
Alcohol	,,	7183	,,
Wood-spirit	,,	5307	,,
Oil of turpentine	,,	10,852	,,
Wax	,,	10,496	,,
Wood	,,	3600	,,
Wood-charcoal	,,	7640	,,
Peat	,,	3000	,,
Compressed peat	,,	4300	,,
Coal (anthracite)	,,	6000	,,
Fat	,,	9000	,,

The absolute heating effect is determined according to the methods of Karmarsch and of Berthier, or by elementary analysis.

Karmarsch's Evaporation Method. According to this method, applied by Dr. Playfair to English coals, by Brix to Prussian, by Hartig and Stein to Saxony coals, the quantity of water is determined which 1 lb. of the fuel will evaporate. According to Regnault's formula, 652 units of heat are required to convert 1 kilo. of water at 0° into steam at 150°. Consequently—

$$1 \text{ kilo. of carbon can evaporate } \left(\frac{8080}{652}\right) = 12{\cdot}4 \text{ kilos. of water}$$

$$1 \text{ kilo. of hydrogen} \quad ,, \quad \left(\frac{34.462}{652}\right) = 52{\cdot}9 \quad ,,$$

Experiments instituted by Dr. R. Wagner and others gave the following results:—

Red beech wood		3·78 kilos. of steam.
Zwickau caking coal	(6·0 per cent ash)	6·45 ,,
Bohemian coal from Nürschau	(19·0 ,,)	5·58 ,,
Forge or smith's coals from Saarbrück	(21·5 ,,)	6·06 ,,
Ruhr coals	(5·5 ,,)	6·90 ,,
Cannel coal	(4·0 ,,)	7·74 ,,

Berthier's Reduction Method. According to the law of Welter (which, however, is not confirmed by experience, since recent researches have proved that, especially as regards hydrogen, great deviations from the law exist), the quantities of heat evolved from different kinds of fuel are relatively proportioned as the quantity of oxygen required for their combustion. Assuming this to be correct, it is easy to ascertain the absolute calorific effect of fuel if its composition is known, it being only required to calculate the amount of oxygen which will effect the complete combustion of the constituents of the fuel, careful account being taken of the oxygen it contains. Practical experience has proved that Berthier's method yields results which, owing to a constant error, are about one-ninth below the truth. The fuel to be tested by this method is finely pulverised, and 1 grm. is mixed with a quantity of litharge slightly more than required for the complete reduction to metallic lead, the minimum quantity being 20, and the maximum 40 grms. This mixture is put into a fire-clay crucible, and covered with a layer of 20 to 40 grms. of litharge. The crucible is covered with another crucible and placed in a charcoal fire, where it is gradually heated. When the contents of the crucible are fused the fire is increased for a few minutes, and the crucible then cooled and broken up in order to obtain the lead button, which is usually clean. This experiment has to be repeated with the same kind of fuel two to three times, and the results should not differ from each other more than 0·1 to 0·2 grm. G. Forchhammer employs instead of litharge a mixture of 3 parts of that oxide with 1 part of chloride of lead (consequently an oxychloride of lead), which mixture previous to use is fused in a crucible, and after cooling, pulverised. Pure wood-charcoal yields, when ignited with litharge or with oxychloride of lead, 34 times its weight, and hydrogen 103·7 times its weight of metallic lead; the hydrogen, therefore, rather more than three times as much as the charcoal (carbon). By means of these data it is possible to estimate the absolute calorific effect of any kind of fuel. As 1 part of carbon can by its combustion raise the temperature of 8080 parts of water 1°, and as pure carbon yields, according to Berthier, 34 parts of lead, every part of lead reduced by the fuel under examination is equivalent to $\left(\frac{8080}{34}\right) = 237{\cdot}6$ units of heat. The application of Berthier's method is suited only to fuel which contains but a small quantity of hydrogen, owing, as already observed, to the incorrectness of the law of Welter; and the method is not applicable to fuel which becomes decomposed below red heat, as in this case a portion of the gaseous matter evolved does not react upon the lead.

Example:—1 grm. of compressed peat yields 17·76 grms. of lead, equal to 4124·5 units of heat (since $237{\cdot}6 \times 17{\cdot}76 = 4124{\cdot}5$); in other words, 1 kilo. of compressed peat yields 6·3 kilos. of steam at 150° (since $\frac{4124{\cdot}5}{652} = 6{\cdot}3$).

Elementary Analysis. Although it has been proved that, as regards isomeric organic bodies, the quantity of heat evolved by their combustion is not précisely proportional to the quantity of oxygen* required for that combustion; and whereas the same quantity of oxygen may yield, under different conditions, different quantities of heat, it may still for all practical purposes be assumed, that as regards fuel of the same or similar composition, the results of elementary analysis give the means of ascertaining the calorific value of such fuel, provided the quantity of ash it contains be first determined.

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* The composition of butyric acid and of acetic ether is the same, and is expressed by the formula $C_4H_8O_2$; yet the former yields on combustion 5647 units of heat, and the latter 6292.

Example:—1 grm. of compressed peat yielded on analysis 0·4698 grm. of carbon, and 0·0143 grm. hydrogen, equivalent to 4288·7 units of heat; because—

$$\begin{array}{lr} \text{Carbon, } 0{\cdot}4698 \,.\ \ 8080 = & 3795{\cdot}9 \\ \text{Hydrogen, } 0{\cdot}0143 \,.\ \ 34{,}462 = & 492{\cdot}8 \\ \hline & 4288{\cdot}7 \end{array}$$

The compressed peat contained—

$$\left.\begin{array}{l} 15{\cdot}50 \text{ per cent of hygroscopic water, and} \\ 31{\cdot}78 \quad \text{,,} \quad \text{chemically combined water} \end{array}\right\} = 48{\cdot}28 \text{ per cent water.}$$

Requiring for evaporation 255·3 heat-units; hence 4288·7 − 255·3 = 4033·4 units of heat. The evaporating power of the compressed peat is therefore—

$$\frac{4033{\cdot}4}{652} = 6{\cdot}19 \text{ kilos.}$$

Stromeyer's Test. According to this method (1861) the fuel is ignited with oxide of copper, the residue treated with hydrochloric acid and chloride of iron, whereby the latter is partly reduced to protochloride, which is estimated by permanganate of potash. This method yields very correct results, but is rather tedious.

Specific Calorific Effect. By specific calorific effect we understand the relative quantities of heat evolved by equal bulks of different kinds of fuel. The specific calorific effect is obtained by multiplying the absolute calorific effect by the specific gravity of the fuel under trial.

Pyrometrical Calorific Effect. The pyrometrical calorific effect of a fuel is that indicated by the temperature resulting from its complete combustion. As there does not exist any pyrometer the indications of which are sufficiently reliable to be converted into thermometrical degrees, we have to content ourselves for the present with an approximative knowledge of the pyrometrical calorific effect as deduced from calculation. The pyrometrical effect of a fuel is equal to the heat-units of absolute heating effect divided by the sum of the relative quantities by weight of its products of combustion, each of these quantities by weight being multiplied by the corresponding specific heat. The flame-yielding substances of the combustible matter of wood and coals are, therefore, possessed of a lower pyrometrical effect than the non-inflammable carbonised substances; while in reference to the absolute calorific effect, the reverse obtains. This is due to the fact that the aqueous vapour formed by the combustion of hydrogen takes up nearly four times as much heat to acquire a certain temperature as does carbonic acid. The difference of pyrometrical effect of fuels is far greater when they are burnt in oxygen than when they are burnt in air. In order to approach in practice as nearly as possible the pyrometrical effect of theory, it is necessary to burn all the carbon completely to carbonic acid, because the temperature of its combustion to carbonic oxide amounts in air to only 1427°, with 2480 units of heat; while if the carbon is burnt to carbonic acid the temperature rises to 2458°, with 8080 heat-units. This complete combustion may be greatly promoted by proper treatment of the fuel; for instance, by keeping wood-charcoal and coke in drying houses for a considerable time; by compressing peat to increase its density; by preparing dense coke; heating the fuel previous to introducing it into the furnace; by the use of heated air; and, lastly, by effecting the combustion with compressed air.

The temperature of combustion is not only the product of the act of combustion itself, but is essentially modified by the action of the active principles of the air during the combustion. For complete combustion there are required:—

For 1 kilo. of carbon, at 15°, 9·7 cubic metres of air.
" 1 " " hydrogen, at 15°, 28·0 " " "

From these data we deduce the following quantities of air as required for the complete combustion of the subjoined quantities of fuel:—

1 kilo. of wood (with 20 per cent of hygroscopic water) = 5·2 cubic metres of air.
1 " wood-charcoal ... ... = 9·0 " " "
1 " pit-coal ... ... = 9·0 " " "
1 " coke ... ... = 9·0 " " "
1 " brown-coal ... ... = 7·3 " " "
1 " peat ... ... = 7·3 " " "

In practice on the large scale these quantities of air require to be doubled in order to obtain complete combustion.

Mechanical Equivalent of Heat. The law of the conservation of energy teaches that heat can be converted into labour, and inversely labour into heat; and that 1 unit of heat corresponds to 424 metrical kilos. of labour. When heat does work it is dispersed in the proportion of 424 units of work for 1 unit of heat; consequently the number 424 expresses the mechanical equivalent of heat. By a foot-pound is understood the force required to lift a weight of 1 pound 1 foot high. When instead of the pound the kilo., and instead of the foot the metre are taken, the term kilogrammetre is employed. 1 kilogrammetre = 6·37 Rhenish foot-pounds; 1 English foot-pound is equal to 0·13825 kilogrammetre; 75 kilogrammetres = 542 English foot-pounds; 1 horse-power (33,000 pounds lifted 1 foot high in 1 minute) is equal to 76·0390 kilogrammetres; 1 unit of heat per English pound is equal to $\frac{5}{9}$ths of a French calorific unit per kilo. The starting-point of the mechanical theory of heat is the axiom first put forward by R. Clausius, that "in all cases in which heat does work a proportional quantity of heat is dispersed or consumed, and inversely, by the performance of an equal amount of work, the same quantity of heat can be regenerated."

Wood.

Wood. Wood consists of several structurally different parts, which may be seen in the transverse section of the wood, viz.:—The axis, or pith, a rather spongy, regularly shaped tissue of parenchyma cells, which radiate towards the bark. This is surrounded by the wood, consisting of an aggregation of bundles of vascular tissue. The wood is surrounded by the bark, and between wood and bark is deposited a very thin layer of cells filled with a turbid fluid, from which the further growth of the tree proceeds by the gradual deposition of newly formed cells towards both the wood and bark side. The bark is externally covered with a layer of peculiarly shaped cells, which with the rind form the bark, covered by, in young trees, epidermis. The pith-cells become obliterated in old trees, and leave a hollow tube. The wood-cells become thicker by the deposition of cellulose, and as this deposition increases in spring but decreases in summer and autumn, the effect is the formation of the so-called annual rings, which are separated from each other by the more compact and harder layers deposited in autumn. The wood-cells are internally hollow, and are separated from each other by intercellular meatus, which contain usually air, but sometimes also gum, resin, &c. The largest quantity of cellulose is deposited in the wood and vascular cells, which essentially constitute the wood; the wood is the harder and more compact, when in a given space the cellulose is deposited in larger quantity, while in the so-called soft wood the walls of the cells are thinner and their number smaller in a given space. The trees of which the wood is used as fuel in Central Europe are:—

Leaved trees.		
Oak (*Quercus pedunculata* and *robur*) ...	fit for felling in	50— 60 years.
Red beech (*Fagus sylvatica*)	,, ,,	80—120 ,,
White beech (*Carpinus betulus*)	,, ,,	110—120 ,,
Elm tree (*Ulmus campestris* and *effusa*) .	,, ,,	20— 30 ,,
Ash tree (*Fraxinus excelsior*)	,, ,,	20— 30 ,,
Alder (*Alnus glutinosa* and *incana*) ...	,, ,,	20— 30 ,,
Birch (*Betula alba* and *pubescens*)	,, ,,	20— 25 ,,
Coniferous trees.		
White fir (*Pinus abies*)	,, ,,	50— 60 ,,
Red fir (Scotch fir) (*Pinus picea*)	,, ,,	70— 80 ,,
Common fir (*Pinus sylvestris*)...	,, ,,	80—100 ,,
Larch or larix tree (*Pinus larix*)	,, ,,	50— 60 ,,

Oak, beech, elm, birch, and ash, are hard woods. Sycamore, larch, and common fir are half-hard; while poplar, lime tree, willows, are soft woods.

Constituents of Wood. Wood essentially consists of woody fibre, small quantities of ash and sap, and a variable quantity of hygroscopic water. Woody fibre, or cellulose, constitutes about 96 per cent of dry wood, and is composed of $C_6H_{10}O_5$; in 100 parts, of—Carbon, 44·45; hydrogen, 6·17; oxygen, 49·38. The vegetable sap consists chiefly of water, but contains organic as well as inorganic matters, partly in solution and partly suspended. The inorganic constituents of the sap (the ash left after the incineration of the wood) are the same in all kinds of wood (see p. 123). In practice it is assumed that wood leaves about 1 per cent of ash; but there is a difference for certain portions of the tree, the trunk yielding about 1·23 per cent of ash, the branches and knotty parts 1·34 and 1·54, and the roots 2·27 parts of ash respectively.

The quantity of water contained in wood is generally larger in soft than in hard woods. 100 parts of wood recently felled are found to contain on an average the following quantities of water:—

Beech	18·6	Common fir	39·7
Birch	30·8	Red beech	39·7
Oak...	34·7	Alder	41·6
Oak (*Quercus pedunculata*) ...	35·4	Elm	44·5
White fir	37·1	Red fir	45·2

Air-dry wood may be considered as consisting of:—

40 parts of carbon (inclusive of 1 part ash).
40 ,, ,, chemically combined water.
40 ,, ,, hygroscopic water.

Wood dried at 130°—at which temperature all the hygroscopic water is driven off—is composed of:—

50 parts of carbon (inclusive of 1 part ash).
50 ,, ,, chemically combined water.

Air-dry beech wood, as used for fuel, contains in 100 parts:—

Carbon	39·10
Hydrogen	4·90
Oxygen	36·00
Water and ash	20·00
	100·00

Heating Value of Wood. The heating value of soft wood is greater than that of hard wood. The wood from coniferous trees is, on account of the resin it contains, the most readily inflammable. Birch wood is very similar to coniferous wood. Resinous woods yield the longest flame. According to Winkler's researches on the heating power of the various kinds of wood, it appears that for 1 klafter of red fir wood might be substituted:—1·07 klafter of lime-tree wood, 0·94 klafter of common fir, 0·92 klafter of poplar, 0·91 klafter of willow wood, 0·89 klafter of tanne, 0·70 klafter of beech, 0·665 klafter of birch, 0·65 klafter of sycamore, 0·635 klafter of elm, 0·59 klafter of oak.* Scheerer assumes that the absolute calorific effect of the different varieties of uniformly dried wood is the same, and that the specific caloric effect of wood containing the same amount of hygroscopic moisture is proportionate to the specific gravity. The pyrometric heating effect of kiln half-dried wood, with 10 per cent of moisture, is, according to Scheerer, = 1850°; while that of fully kiln-dried wood is = 1950°. According to Péclet, the combustion of clean dry wood evolves a temperature of 1683°, provided the oxygen of the air supplied for combustion be all consumed, for if that is not the case, or only half the oxygen be consumed, the temperature is only 960°, as happens in stoves of the ordinary construction.

According to Brix's investigations, the evaporative power of different kinds of wood is as subjoined:—

		Undried. Per cent.	Dried. Per cent.
Fir wood, containing water, per cent	16·1	4·13	5·11
Elm wood, " "	14·7	3·84	4·67
Birch, " "	12·3	3·72	4·39
Oak, " "	18·7	3·54	4·60
Red beech, " "	22·2	3·39	4·63
White beech, " "	12·5	3·62	4·28

That is to say, 1 kilo. of fir wood, containing 16·1 per cent of water, evaporates 4·13 kilos. of water.

Wood Charcoal. Nearly all organic compounds become decomposed by heat, and leave carbon if access of air is prevented. If the escape of gases and volatile vapours evolved when wood is submitted to dry distillation is permitted, a residue is left known as wood-charcoal. Among the volatile products of this operation are gaseous substances, such as carbonic acid, carbonic oxide, and marsh-gas, while the condensable portion of the volatile products consists of tar and an aqueous fluid. This latter consists of crude pyroligneous (acetic) acid (see p. 469) and of wood-spirit. The tar contains a large number of fluid and solid substances, among which are paraffin, creosote (oxyphenate of methyl), oxyphenic and carbolic acids (that is to say, true carbolic acid, cresylic acid, and phlorylic acid), and several hydrocarbons;

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* A klafter is a cubical measure = 108 cubic feet.

all these substances are combustible. The following diagram exhibits the chief products of the dry distillation of wood:—

Wood.			
a. Real wood. *b.* Hygroscopic water.	. Illuminating gas.	Acetylen. Elayl. Benzol. Naphthalin (?)	Carbonic oxide. Carbonic acid. Marsh-gas. Hydrogen.
	β. Tar.	Benzol. Naphthalin (?) Paraffin. Reten. Carbolic acid.	Oxyphenic acid. Cresylic acid. Phlorylic acid. Empyreumatic resins. Creosote.
	γ. Pyroligneous acid.	Acetic acid. Propionic acid.	Aceton. Wood spirit.
	δ. Wood charcoal.		

Carbonisation of Wood. Wood is carbonised chiefly for the purpose of concentrating the fuel or combustible matter it contains, to obtain a more readily transportable material, and for the purpose of converting the wood into a fuel for use in metallurgical and technical processes in which wood, as such, cannot be employed.

Wood may be carbonised with the sole view of making tar (Stockholm tar), or with that of making wood-gas or charcoal. In the latter case the wood is very frequently carbonised in the forests where it is felled, in heaps, pits, or ovens.

Carbonisation in Heaps. A regularly constructed heap of blocks of timber covered with a layer of earth and charcoal-dust is formed, the wood being placed vertically or horizontally as regards the direction of the axis of the heap. In the first case the heap is termed a "standing," in the other a "laid" heap. The axis is a pole or several poles of wood.

Construction of the Heap. The building of the heap is commenced by putting up the axis pole or poles. Vertical heaps are, according to their construction, distinguished in Germany, as:—*a.* Wälsh heap, Fig. 301. *b.* Slavonian heap, Fig. 302. *c.* Schwarten heap, Fig. 303.

The Wälsh, or Italian heap (Fig. 301) is constructed with a hollow central support of planks or stout laths, kept apart from each other by the balks, *n.* The heap contains two or three layers of wood and is conical in shape. The layer of earth on the wood is termed the chemise. In the lower part of the hollow pole or shaft resinous wood is placed for kindling the pile.

Fig. 301.

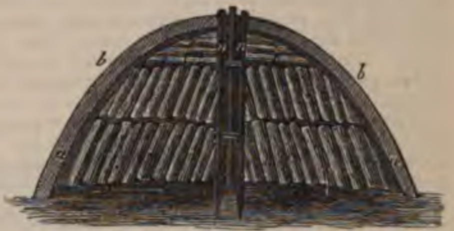


Fig. 302.

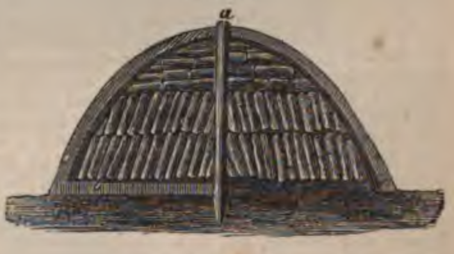
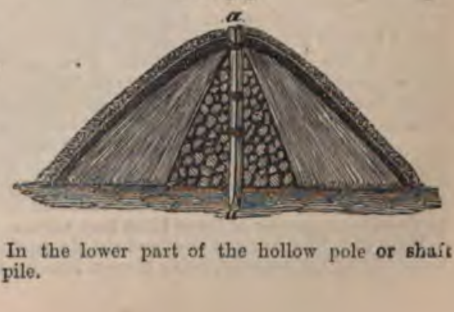


Fig. 303.



The Slavonian heap (Fig. 302) is distinguished from the former by the fact that the axis is a solid pole and by the channel, *b*, by means of which the wood is fired. A third kind of vertical heap, termed the Schwarten, is in use in Norway, the name being derived from the word "Schwarten," signifying irregular. Three of the larger logs form the central pole, *a a*, round which light combustible material is placed for the purpose of kindling the heap; while the blocks of wood are next built up. The horizontal heaps have the outward appearance of the former, but the blocks of wood are placed horizontally and radially. The pole or axis is a solid shaft, and air holes or channels are made in the wood. In order to prevent the layer of earth which covers the heap falling in and choking the progress of the smouldering fire, a layer of leaves and twigs is first placed on the wood, and on that the earth, mixed with charcoal-dust. At first the heap of wood is not quite covered with earth, an uncovered space of some 6 to 12 inches being left at the foot of the heap for the purpose of admitting air. The layer of earth usually has a thickness of 3 to 5 inches, but at the top it is thicker. In order to protect the heap from the effects of strong wind, it is usual to put up what are termed wind-blinds, simply planks of wood placed close together and supported by stout poles.

There are two methods in use for kindling or firing the heaps of wood:—1. Kindling at the bottom, access to the centre of the heap being obtained by a channel, into which ignited straw is introduced. 2. Ignition from the top, or roof, by throwing into the central shaft ignited charcoal and wood-shavings.

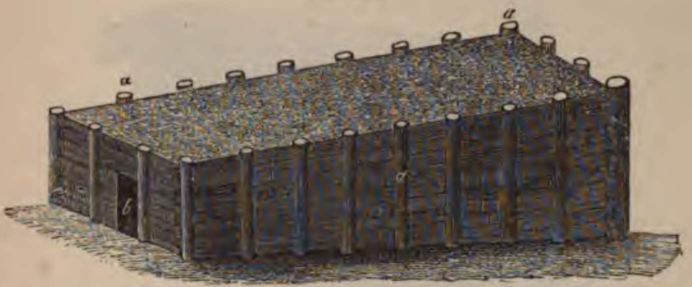
Charcoal Burning. We have to distinguish three stages or phases in this operation:—1. The sweating. 2. The full combustion. 3. The slow smouldering. In order that the fire may spread through the heap, it requires at first a more plentiful supply of air, and for that purpose the heap is left entirely uncovered, or at least left open at the bottom. The first effect of the firing is that a large quantity of watery vapour and products of dry distillation are formed within the heap, which becomes consequently wet, or begins to sweat. During this time there is the risk of explosion of the mixture of air with hydrocarbon gases and vapours, by which explosion the overthrow of the heap, or if not so violent, a shaking of the covering layer of earth, may take place. It may happen, also, that at this period the combustion becomes internally so active as to completely consume more or less of the wood. Any holes which may be observed externally are at once filled up with earth, grass, wet wood, clay, or any suitable material. When the vapours issuing from the bottom of the heap become brighter in colour, complete ignition of the wood has commenced, and it then becomes necessary to prevent the access of air by covering the entire heap with earth mixed with charcoal-powder; this operation is termed the encompassing (*umfassen*) of the heap, which is left in that condition for three, four, or six days, the high temperature being sufficient to complete the carbonisation of the wood without further access of air. In order to insure the complete carbonisation of the outer portions of the heap, the combustion must be carefully conducted from the top and centre outwards by partially removing the covering layer towards the bottom, and by making small channels at various parts of the covering, an operation known as the slow smouldering or burning off. When the smoke which issues from the channels becomes bright and blue-coloured, the charcoal is well burnt, and therefore the channels and apertures are all closed with earth, in order to extinguish the fire. In this condition the heap is left for twenty-four hours. Then the layer of earth is raked off, and dry earth thrown on the heap for the purpose of filling the interstices between the still red-hot charcoal, which becomes gradually extinguished. As soon as the heap is quite cold externally, it is once or twice gently watered by means of a watering-pot, then broken up, and the charcoal taken out.

Carbonisation in Beds. This mode of charcoal-burning is in use in Southern Germany, Russia, and Sweden, and is a continuous operation in so far as the wood is gradually carbonised, fresh green wood being added while the charcoal is withdrawn. The wood is sawn into logs and not hewn to smaller blocks. The carbonisation-bed is a rectangular wooden box, Figs. 304 and 305, the latter being a vertical section. The bed is, in fact, a kind of kiln, of which *a a* are the poles and outer logs, *h* the covering layer of earth, *b* the hearth. While the slow combustion proceeds from *b* towards the opposite end, the charcoal formed is gradually withdrawn. The burner, or workman, has to see that the combustion proceeds regularly and keeps parallel to the sides of the bed.

Carbonisation in Ovens or Kilns. This process is an imitation in brickwork of the carbonising process in heaps, because the carbonisation of the wood is effected by the combustion of a portion of wood of the heap. The oven, or kiln, admits of a more perfect collection of the products of the dry distillation—tar, pyroligneous acid, &c.,—but the charcoal is not quite so good as that obtained by the preceding methods. The shape and mode of construction of these kilns may vary, as will be presently seen.

Fig. 306 exhibits one of the most simply constructed kilns. The wood is placed either vertically or horizontally, being thrown into the kiln through the opening, *a*, or carried in through the doorway, *b*, which also serves as the channel through which the firing of the wood is performed. During the ignition all the apertures of the kiln are closed with brickwork, with the exception of a small opening at *b* and at *a*. The small apertures seen at the top of the kiln are intended for the escape of the smoke.

FIG. 304.



In the kiln exhibited at Fig. 307, the doorways, *a* and *b*, are intended for the introduction of the wood, and *b* also for withdrawing the charcoal. *c c c* are draught-holes provided with plugs. The iron pipe, *d*, is intended for carrying off the volatile products of the dry distillation. During the operation *a* and *b* are closed with brickwork or with tightly-fitting iron doors lined with fire-clay slabs. The tar is collected in a reservoir. Below *b* a small aperture indicates the mouth or outer opening of the firing channel.

FIG. 305.

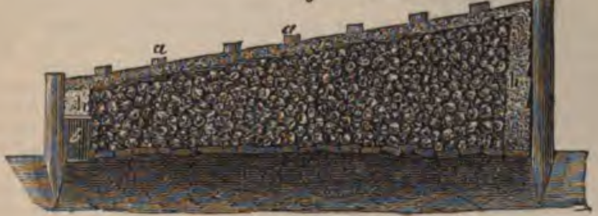
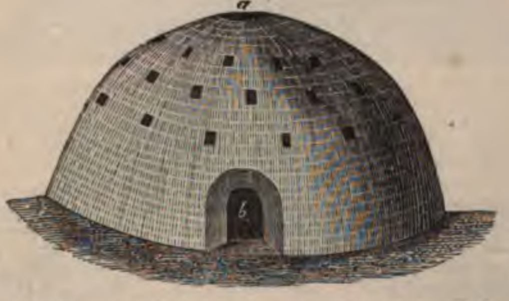


FIG. 306.



The kiln represented in Fig. 308, in vertical section, is constructed for the admission of air through the ash-pit, *e*, and fire-bars, *r*; the wood is introduced through *a* and *b*; *q* is the pipe for carrying off the volatile products.

Carbonisation of Wood in Ovens. The carbonisation of wood is also effected in closed vessels:—1. Retorts. 2. In tubes or cylinders, heated air, blast-furnace gases, or superheated steam being sometimes used for the purpose of carbonising the wood. As regards the carbonisation of wood in retorts, this is effected by placing the wood in cast-iron or fire-clay retorts, which are heated externally, and are provided with pipes for conveying away the volatile products of the carbonisation, this process being carried on chiefly for obtaining tar or wood-gas. In the case of tubular kilns, the firing of the wood is effected by the aid of a series of iron tubes, placed in the kiln and connected outside with a source of heat as well as with a chimney-stalk. The hot air and flame of a furnace are passed through these tubes, or may be directly led into the kiln, provided the hot air and flame are deprived of their oxygen. Upon these principles is constructed the kiln invented by Schwarz, and known as the Swedish kiln, of which Fig. 309 exhibits a vertical section. *b* is the carbonisation space enclosed by the brickwork, *a*. Through the apertures, *c c*, the hot air is admitted which effects the carbonisation. The liquid products of the dry distillation are collected on the sloping floor of the kiln and conveyed by means of the syphon-tubes, *e e*, into the tar-vessels, *f f*. The vapours of the vola tile fluids (pyroligneous acid, wood-spirit, &c.), pass through the tubes, *g g*, into the condensing vessels, *h h*, which are connected with a high chimney (see *i*, Fig. 310), to aid

Fig. 307.

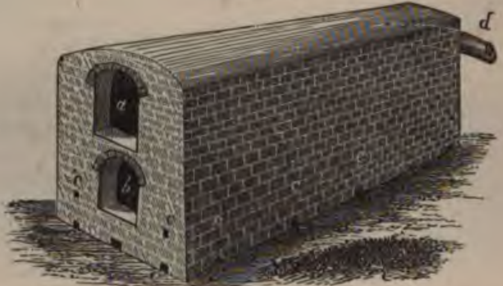


Fig. 308.

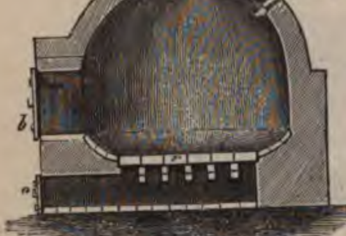
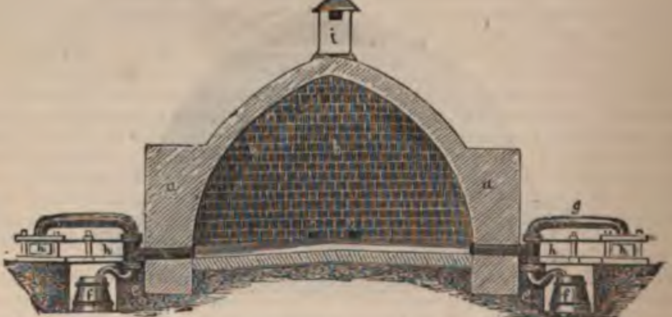


Fig. 309.



the draught of the apparatus. The openings, *d d*, serve for the introduction of the wood. There are no fire-bars in the hearth of this kiln.

The carbonisation of wood with the view of producing tar is best effected by the method in general use in Russia, of which Hessel has given (1861) the following description. The wood, generally of coniferous trees, is cut up with an axe, being distinguished as Brawican and Luczina; the former wood from the trunk of the trees, the latter the knotty roots. The wood is heaped up on a plot of ground, Fig. 311, which is somewhat elevated above the level of the soil, and is funnel-shaped, the whole being constructed of clay and lined with roofing-tiles, on which the tar collects and flows off into a vessel placed in the vault, as exhibited in the cut. The wood is heaped in six to eight layers, and is first covered with hay or dung, next with a layer of a few inches in thickness of sand or earth. The wood in the heap is ignited at the bottom, where forty to fifty apertures are left in the covering, these apertures being closed with wet sand as soon as the combustion of the wood becomes active, and has spread through the whole heap. After about six days' smouldering, the top of the heap falls in and a strong flame bursts out. After ten to twelve days the tar begins to collect and is removed daily. The smouldering of the wood continues for three to four weeks; the quantity of charcoal obtained is very small. According to Thenius, wood-tar is obtained by a similar process in Lower Austria from the wood of the black fir, which does not yield turpentine; but in Bohemia a very resinous wood is used for tar-making. 100 parts of fir wood yield in Russia 17·6 parts of tar and 23·3 parts of charcoal.

Fig. 310.

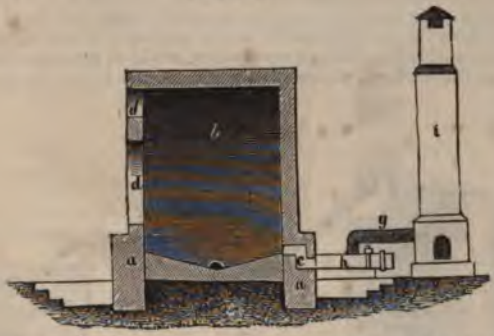
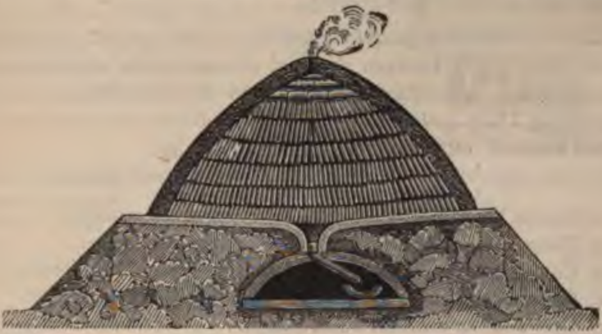
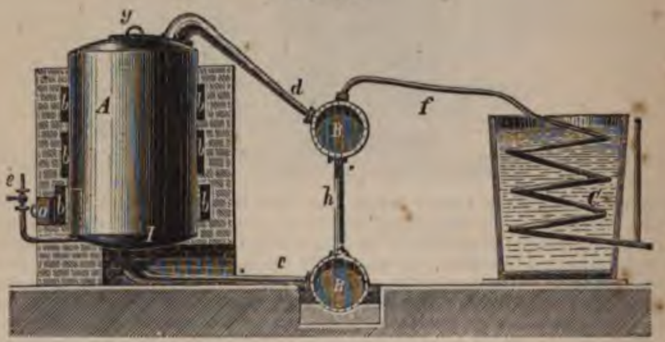


Fig. 311.



Since the year 1853 there has been in use in Sweden an apparatus for the distillation of tar from wood, known as a thermo-boiler. According to Hessel's description, this apparatus consists of a boiler-shaped iron vessel, A, Fig. 312, of about 8 cubic metres capacity, and fitted with a man-hole for introducing the wood. This vessel is heated by a fire at *a*, and the flues, *b b*. In order to heat the wood rapidly to 100°, a jet of steam is forced into the vessel through *e*. The tar which might collect and condense in the vessel is carried off by the aid of the pipe *c* to B, while the vapours of tar and other volatile products are conveyed through *d* into B'. The matter there condensed flows through *h* to B, while the more volatile products are rendered liquid in the condenser, C. The combustible gases are returned to the fireplace. In addition to tar, there are, at the outset of the operation, also obtained oil of turpentine and pyroligneous acid. The charcoal, which is extinguished by means of steam, is removed from the boiler by the opening *a*. According to an investigation by Thenius (1865), with the view of ascertaining whether the tar obtained in making wood-gas is equally fitted for naval purposes and for boiling down to pitch as the tar obtained by other methods, it was found that such is not the case. This agrees with Dr. Owden's researches, made at his extensive acetic acid and wood-spirit works at Sunderland, where the tar obtained is burnt, or used with lime and fire-clay for making a kind of asphalte. Owing to the cheapness of coal in the locality, the wood-charcoal is almost a waste product.

FIG. 312.



Properties of Charcoal. We distinguish between hard wood and soft wood charcoal, and as regards the latter, again between charcoal obtained from leaf-bearing trees and from coniferous trees. According to the degrees of carbonisation, we distinguish between well-burnt black-coal and the so-called *charbon roux*, a more or less deep brown torrified charcoal, often used in gunpowder making.

According to the size, charcoal is—at least abroad—divided into :—

1. Coarse log-coal, the largest and most compact lumps.
2. Forge-coal, compact lumps about 4 inches diameter.
3. Coal from the centre of the heap, small lumps and porous.
4. Small coal, nut and pebble-sized lumps, mixed with dust.
5. Raw coal, or not well-burnt lumps.

As regards the yield of charcoal by bulk, this may be referred either to the real volume of the mass, after deduction of interstices present in the heap, or to the apparent volume without that deduction being made. We can compare :—

a. The apparent volume of the wood with the apparent volume of the charcoal.
b. The real volume of the wood with the real volume of the charcoal.
c. The real volume of the wood with the apparent volume of the charcoal.

The first method may be called the production according to the apparent volume (I.); the second, the yield according to the real volume (II.); the third, the yield according to both volumes (III.) :—

Method (I.) gives the following results:—

Oak wood	71·8—74·3	per cent charcoal.
Red beech wood	73·0	,, ,,
Birch wood	68·5	,, ,,
Dwarf beech wood (as grown for hedges abroad)	57·2	,, ,,
Fir wood	63·6	,, ,,

According to the real volume (II.) the average of several experiments gave a yield of 47·6 per cent. According to both volumes (III.), the following results were obtained at Eisleben:—

	Weight.	Apparent volume.	Both volumes.
Oak wood	21·3 per cent	71·8 per cent	98·7 per cent
Red beech wood	22·7 ,, ,,	73·0 ,, ,,	100·4 ,, ,,
Birch wood	20·9 ,, ,,	68·5 ,, ,,	94·2 ,, ,,
Dwarf beech wood	20·6 ,, ,,	57·2 ,, ,,	78·6 ,, ,,
Fir wood	25·0 ,, ,,	63·6 ,, ,,	87·2 ,, ,,

Composition of Wood-Charcoal.

Omitting the small quantities of hydrogen and oxygen present in charcoal, its average composition in air-dry state is the following:—

Carbon	85 per cent
Hygroscopic water	12 ,, ,,
Ash	3 ,, ,,

Combustibility and Heating Effect.

The combustibility of freshly burnt charcoal is very great, for it continues to burn, with proper access of air, when once ignited; but as charcoal does not contain any volatile combustible matter, it requires a great heat to become ignited, more especially as it is a very bad conductor of heat.

The heating effect of various kinds of wood-charcoal is shown by the figures of the subjoined table, the heating effect of carbon being taken as the unit:—

	Absol.	Specif.	Pyrom.	1 part of charcoal reduces of lead.	1 part of charcoal heats water from 0°—100°.
Well-burnt charcoal, air-dry	0·97	—	2450	—	On an average 75·7 parts.
Well-burnt charcoal, quite dry ...	0·84	—	2350	—	
Birch wood ,, ,, ...	—	0·20	—	33·71	
Ash wood ,, ,, ...	—	0·19	—	—	
Red beech wood ,, ,, ...	—	0·18	—	33·57	
Red fir wood ,, ,, ...	—	0·17	—	33·51	
Sycamore wood ,, ,, ...	—	0·16	—	—	
Oak wood ,, ,, ...	—	0·15	—	33·74	
Alder wood ,, ,, ...	—	0·13	—	32·40	
Linden wood ,, ,, ...	—	0·10	—	32·79	
Fir tree ,, ,, ...	—	—	—	33·53	
Willow wood ,, ,, ...	—	—	—	33·49	

The evaporative power of fir wood charcoal containing 10·5 per cent of water and 2·7 per cent of ash amounts to 6·75 kilos., viz., 1 kilo. of the charcoal evaporates 6·75 kilos. of water. This charcoal, in perfectly anhydrous state and with 3·02 per cent ash, evaporates 7·59 kilos. of water.

Charbon Roux; Torrified Charcoal.

As the complete carbonisation of wood entails a loss of about 40 per cent of fuel, it has been recently tried to prepare a kind of charcoal exhibiting a brown-black colour, and obtained from wood by torrifying rather than by carbonising it, experience having shown that such a charcoal is obtained when the air-dry wood has lost by torrifying some 60 to 70 per cent of its weight. This kind of charcoal is intermediate to real black charcoal and kiln-dried wood; it contains more oxygen, is readily pulverised, but is less porous than either kiln-dried wood or ordinary charcoal, than which it is far more inflammable, and is hence preferred in gunpowder making. Charbon roux, or torrified charcoal, is a very useful and important fuel for industrial and metallurgical purposes.

Freshly prepared torrified charcoal has the following composition:—

Carbon...	74·0 per cent
Chemically combined water	24·5 ,, ,,
Ash	1·5 ,, ,,

The composition of this charcoal after keeping is:—

Carbon...	66·5 per cent.
Chemically combined water	22·0 ,, ,,
Hygroscopic water	10·0 ,, ,,
Ash	1·5 ,, ,,

Roasted Wood; Bois Roux. The Association for Promoting Chemical Industry at Mains prepares an intermediate product to wood and torrified charcoal, to which the name red wood (roasted wood, *bois roux*) is given. It is made from beech wood, and is the by-product of the preparation of acetic acid and creosote. It has all the external appearances of wood, but the colour, which is deep brown. It is highly inflammable, and consists on an average of:—

Carbon	52·66 per cent
Hydrogen	5·78 ,, ,,
Ash	0·43 ,, ,,
Water (moisture or constitutional?) .	4·49 ,, ,,
Oxygen	36·64 ,, ,,

According to R. Fresenius's researches, the evaporative power of air-dry beech wood is to that of *bois roux* as 54·32 : 100.

Peat.

Peat. This is the product of the spontaneous decay of vegetable matter, more especially of marsh plants, mixed with various mineral matters, sand, clay, marl, lime, iron pyrites, iron ochre, &c. Peat is especially formed in places where shallow, stagnant pools of water abound, in which the plants grow, while at the same time the peat is precluded access of air. The following plants are chiefly met with in peat bogs and form the peat:—*Eriophorum*, *Erica*, *Calluna*, *Ledum palustre*, *Hypnum*, and also *Sphagnum*, a plant especially fitted for the formation of peat, because it never wholly dies, but continues to vegetate towards the surface of the water or bog, while the older parts decay.

The different qualities of peat are partly due to the plants from which the peat is formed, but chiefly to the more or less complete decay these plants have undergone, to the mineral substances mixed with the peat, and to the compression to which it has been submitted by the weight of other mineral materials deposited upon it. Abroad, and in countries where peat abounds, several varieties are distinguished, such as—1. Moor peat, chiefly derived from kinds of *Sphagnum*, and found in several parts of the United Kingdom as very young peat—for instance, at Aldershot, and on moor lands. 2. Heath peat, in Holland known as *plaggenturf*, is the surface soil of heather-growing places. 3. Meadow-land peat, decayed coarse grass mixed with a soft subsoil. 4. Wood or forest peat, met with in forests, and formed by the decayed wood, leaves, &c. 5. Marine peat, formed by the decay of sea plants, various kinds of *Fucus*, &c.

Peat is directly obtained by simply cutting it with a spade from the surface of the soil, either with or without the necessity of first removing a layer of other soil, while some peat can be obtained only by dredging for it under water. In the latter case a mud is dredged up which (as happens in Holland, where the land peat is known as *hoog veen*, while the peat from under water is termed *laag veen*), has to be dried gently in open air, and afterwards cut up in brick-shaped lumps, and further air-dried. Peat is often artificially compressed for the purpose of obtaining a more compact fuel. The quantity of water contained in freshly dug peat is very large, and by keeping this peat in dry situations it may lose 45 per cent of its original weight. Assuming the organic matter of peat to consist of—

Carbon	60 per cent.
Hydrogen	2 „
Water	38 „

The best solid air-dry peat consists of—

Solid peat mass (inclusive of ash)	75 per cent.
Hygroscopic water	25 „

or of—

Carbon	45·0 per cent.
Hydrogen	1·5 „
Chemically combined water	28·5 „
Hygroscopic water	25·5 „

The following analyses exhibit the composition of peat-ash, which is characterised by containing a far larger quantity of phosphoric acid than wood-ash.

According to E. Wolff, two kinds of peat-ash from the Mark (*a* and *b*), and another from South Bavaria (*c*, analysed by Dr. Wagner) contain:—

	a.	*b.*	*c.*
Lime	15·25	20·00	18·37
Alumina	20·50	47·00	45·45
Oxide of iron	5·50	7·59	7·46
Silica	41·00	13·50	20·17
Phosphate of calcium and gypsum ...	3·10	2·60	
		Alkali, phosphoric acid, sulphuric acid, &c.	8·55

Drying Peat. The use of peat as fuel and its value as such depend in a great measure upon the quantity of water and the mineral substances it contains. Peat may be more or less dried:—

1. By exposure in stacks in open air, or better in sheds where the peat is protected from rain, but where a free circulation of air obtains. Air-dried peat contains 25 per cent water.

2. By artificial heat, kiln drying at 100° or 120°, in kilns or stoves heated by a distinct fire-place, or by waste heat from other operations.

3. By compressing peat. The compression has the following advantages:—*a.* Rendering the peat more compact and thus increasing its pyrometric effect. *b.* Lessening its bulk, and consequently lessening the cost of transport by water, in which mode of transport the cost is calculated by bulk or cubic measurement. *c.* The compression aids

the drying. The operation of compressing freshly dug peat, simple as it appears, has been found in practice to be accompanied with difficulties which hitherto have not been, and are not likely to be, overcome, for several reasons, among which is the fact that peat, as a heterogeneous material, cannot be dealt with satisfactorily by compression. But a step in the right direction towards the utilisation of the enormous masses of peat soil has been made, by submitting the soil first to a kind of grinding lixiviation, which converts it into a homogeneous mass, from which the greater part of the mineral matters can be eliminated.

In the works at Staltach, near Munich, the following process has been introduced by Weber for preparing peat. The peaty material having been brought from the moor in lumps is put into a kind of pug-mill moved by steam-power, and which reduces the peaty substance to a uniform paste. This paste is moulded, compressed, and dried in a stove. Schlickeysen has invented a machine of improved construction; in its application it is unnecessary to pour any water on the peaty material, consequently the drying process is less tedious and expensive. Dr. Versmann's peat-preparing machine consists chiefly of a funnel-shaped stout sheet-iron vessel provided with small holes on its periphery and internally fitted with an iron core-piece, which bears cutters fastened spirally on its surface. By the action of these cutters the peaty matter is reduced to a pulp, and in that state issues from the holes, while any coarse particles, such as pieces of root, vegetables, &c., are discharged at the lower opening of the funnel-shaped iron vessel. On the Haspel moor peat bog situated between Augsburg and Munich, there has been in use up to the year 1856 a peat-preparing machine, originally invented by Exter, at Munich, and consisting essentially of solid iron cylinders, provided with strong teeth 6 centims. long, and arranged in the same manner as obtains in bone-crushing mills. The peaty material is reduced with the aid of water to a pulp, which is next pressed, moulded, and dried. The unreduced vegetable matter and roots are separated from the peaty mass by the machine. Challeton's peat-preparing machine, invented in 1824, and worked at Montanger, near Corbeil, Seine et Oise, France, consists of a set of cylinders, 1·3 metres in length, and fitted with cutters. The peaty mass is first cut into shreds and is next transferred to another portion of the machinery, in the particulars of its construction very similar to a coffee-mill. With the assistance of some water the peaty material is converted into a pulp, which is next lixiviated, and thus deprived of mineral impurities. The thin, pasty, peaty mass is run into a large tank or pit dug in the soil, and left there until it has acquired sufficient consistency to be moulded. This mode of treating peaty matter has been employed at Rheims and St. Jean on the Bieler Lake, Switzerland. By Challeton's process—100 cwts. of peaty material (*veen*)* yield 14 to 15 cwts. of peat, containing about seven-eighths less ash than in natural state.

It is evident that a process of lixiviation, however suitable in regard to its application to peaty matter, is, in a certain sense, an irrational mode of treating a substance which has to be again dried thoroughly, and which, even after being submitted to the several operations, is not a fuel equal to coal. It is, therefore, a very great improvement in the utilisation of peat-soil that the peaty matter should be treated in a different manner, or by the so-called dry compression process, as carried out by Gwynne and Exter. According to this method the peaty mass is first deprived of its natural excess of water by means of a hydro-extractor; next pulped, and this pulp dried by artificial means; the material obtained is ground to powder, which is finally moulded with the aid of strong pressure and the simultaneous application of heat. The peat thus prepared is of a deep brown-black, a hard, stone-like material, excellently suited for use as fuel, especially for manufacturing and metallurgical purposes. Another process of peat preparation consists in first cutting and drying the peat in air. The air-dried peat is ground to a coarse powder and then dried in a stove. The dried peat is moulded and pressed by means of an eccentric press, heat (50° to 60°) being simultaneously applied. Peats from the Kolber moor (*a*), and from Haspel moor (*b*), thus prepared, were found to contain in 100 parts:—

	a.	*b*.
Ash	4·21	8·34
Water ..	15·50	15·50
Carbon ..	46·98	49·82
Hydrogen ..	4·96	4·35
Nitrogen ..	0·72	26·99
Oxygen ..	27·63	
	100·00	100·00

---

* There is no word in English equivalent to the Dutch *Veen*, a term applicable to all soils which consist either entirely or chiefly of peaty matter. There is no equivalent term also in German, but there is in the Danish and Russian languages.

Heating Effect of Peat. The combustibility and inflammability of peat are, owing to the large quantity of ash and water it contains, less than that of wood.

According to Karmarsch the absolute heating effect of:—

100 kilos. of yellow peat = 94·6 kilos. of air-dry fir wood.
100 „ brown „ = 107·6 „ „ „
100 „ hard „ = 104·0 „ „ „
100 „ pitch „ = 110·7 „ „ „
100 cubic metres of yellow peat = 33·2 cubic metres of fir wood.
100 „ brown „ = 89·7 „ „ „
100 „ hard „ = 144·6 „ „ „
100 „ pitch „ = 184·3 „ „ „

These results agree with those obtained by Brix. Karsten states that for evaporative and boiling operations—

2½ parts by weight of peat are = 1 part by weight of coal
4 parts by volume „ = 1 part by volume „

According to Vogel, the evaporative effect of peat is the following:—

	Water.	Evaporative effect.
Air-dry fibre	10 per cent	5·5 kilos.
Machine-made peat...	12—15 „	5·0—5·5 „
Compressed peat ...	10—15 „	5·8—6·0 „

New Method of Utilising Peat. During the last twenty years peat has been employed for the preparation of paraffin, peat-creosote, and paraffin oil. As far back as the year 1849, Reece tried to utilise Irish peat in the preparation of paraffin; and the experiments of Drs. Kane and O'Sullivan proved that 1 ton of Irish peat yielded about 1·36 kilos. of paraffin, 9 litres of paraffin oil, and 4·54 litres of lubricating oil. According to Wagenmann, the peat of the Isle of Lewis, Scotland, yields from 6 to 8 per cent tar, and this again yields 2 per cent of photogen or paraffin oil, 1·5 per cent of solar oil, and 0·33 per cent of paraffin.

Carbonised Peat.

Carbonised Peat. In many parts of Germany, and of all countries where peat bogs abound, the use of peat as fuel is out of all proportion to the enormous quantity of material left untouched; this is due to the fact that peat is as fuel in many respects a very inferior material. Its bulk in reference to its heating effect is very large; its combustion evolves a very disagreeable odour and pungent smoke, so that peat is therefore not suited for heating rooms. On this account peat is carbonised. As peat varies greatly in composition, the carbonised peat or peat-coke also varies, and the composition of the peat-coke may be represented as follows:—

	Superior quality.	Inferior quality.
Carbon	86	34
Hygroscopic moisture	10	10
Ash	4	56

Nothing is known as to the absolute and specific calorific effect of peat-coke, since no experiments have been instituted. Ordinary peat-coke appears to approximate charcoal in its specific calorific effect, but peat-coke is otherwise inferior to charcoal because it is less dense, and cannot on account of its dusty ash produce an intense heat. Peat-coke is not suited for fuel in blast-furnaces or other metallurgical operations, but answers well for heating steam boilers, evaporating pans, and similar apparatus. But peat-coke made from compressed peat is a highly valuable fuel for metallurgical operations, so that it becomes a matter of importance to find a means of compressing peat inexpensively. In Holland, peat, especially that known as *spon turf*, or *hoogeveensche turf*, is very largely used for industrial purposes, and on account of not containing sulphur is used at the Utrecht mint for melting silver and gold.

Brown-Coal.

Brown-Coal. This mineral fuel is also the product of a peculiar decomposition of wood, but the decay has in this instance been more complete. It is not easy to draw a clear line of demarcation between brown-coal and coal, when only the properties of these substances are to be considered. Therefore the palæontological and geological relations have to be taken into account when it is required to estimate the value of a fossil fuel. In general it may be said that any fossil coal of more recent date than the chalk formation may be termed brown-coal; while all fossil coals found below the chalk formation are really pit-coal. As the latter contain more nitrogen than the former, this fact may be utilised in testing to distinguish between pit-coal and brown-coal. Brown-coal, on being heated in a dry test-tube, yields fumes which exhibit an acid reaction, because brown-coal is somewhat similar to cellulose; whereas, if the same test be applied to pit-coal, ammoniacal fumes are given off (containing ammonia, aniline, lepidin, &c.), which exhibit an alkaline reaction. When finely pulverised pit-coal is boiled for some time with a rather concentrated solution of caustic potash, the fluid remains colourless; but when brown-coal is similarly treated, the liquid becomes brown-coloured by the formation of humate of potash. This test does not, however, apply to the brown-coal found in the tertiary formation of the northern slope of the Alps. E. Richter and Hinrichs state, that when pit-coals are dried at 115°, and caused to lose a very small quantity in weight, this loss disappears again, in consequence of an oxidation which takes place; while if brown-coal is so treated, the subsequent increase in weight is not observed.

According to the various degrees of decay, several kinds of brown-coal are distinguished:—1. Fibrous brown-coal, fossil or bituminous wood, lignite, is similar to wood, the structure of stem, branches, and roots being apparent. 2. Common brown-coal forms compact brittle masses, exhibiting a conchoidal fracture. 3. Earthy brown-coal is a mixture of brown-coal and earthy matter. In several parts of Germany and the Austro-Hungarian Empire, brown-coal of excellent quality is found, especially suited for the purpose of preparing paraffin and paraffin oils.

Brown-coal is frequently found mixed with the rhombic variety of iron pyrites. When that mineral and earthy matter predominate, there is formed what is termed alum-shale, under which name, however, is also known a kind of clay mixed with bitumen and iron pyrites. The average quantity of ash contained in brown-coals amounts to 5 to 10 per cent. The ash contains chiefly alumina, silica, lime, magnesia, oxides of iron and manganese; while the quantity of hygroscopic moisture in freshly dug brown-coal may amount to 50 per cent. The substance contains in air-dry state 20 per cent water, and the average composition of brown-coal may therefore be quoted as:—

Carbon	48—56	per cent.
Hydrogen...	1—2	"
Chemically combined water	31—32	"
Hygroscopic water	20	"

The combustibility of brown-coal is less than that of wood, while its inflammability varies between that of wood and pit-coal. The heating effect of brown-coal is with—

	Hygroscopic water. Per cent.		Ash. Per cent.	Absol.	Specif.	Pyrom.
Air-dry fibrous brown-coal, containing	20	and	0	0·48	0·55	1800
„ „ „ „	20	„	10	0·43	—	—
„ earthy „ „	20	„	0	0·61	0·79	1975
„ „ „ „	20	„	10	0·55	—	—
„ conchoidal „ „	20	„	0	0·69	0·88	2050
„ „ „ „	20	„	10	0·62	—	—
Kiln-dried fibrous brown-coal „	20	„	0	0·61	—	2025
„ „ „ „	20	„	10	0·55	—	—
„ earthy „ „	20	„	0	0·76	—	2125
„ „ „ „	20	„	10	0·69	—	—
„ conchoidal „ „	20	„	0	0·85	—	2200
„ „ „ „	20	„	10	0·76	—	—

It appears from this table that the absolute and pyrometric calorific effect of air-dry brown-coal is more than twice that of kiln-dried wood; and this remark applies to the specific calorific effect of brown-coal, which is more than twice that of the best wood.

The evaporative effect of brown-coal is the following:

	Water.	Ash.	Evaporative effect.
Bohemian brown-coal	28·7 per cent.	10·6 per cent.	5·84 kilos.
Bituminous wood ...	23·7 „	3·9 „	5·76 „
Earthy coal	47·2 „	4·8 „	5·55 „
Lump coal	47·7 „	3·1 „	5·08 „

Brown-coal as Fuel. Brown-coal is a less suitable fuel and its applications are far more limited than those of pit-coal, for brown-coal cannot be used in those cases where a caking coal is required. Brown-coal is useful as fuel for certain chemical operations—distillation, evaporation, &c.—and may be used for heating rooms in dwelling houses, when burnt in well-constructed stoves. Earthy brown-coal is not well fitted for use as fuel, unless it has first been lixiviated with water, moulded into bricks, compressed, and dried. It has been found in practice that brown-coal freshly dug is a better fuel than brown-coal which has been exposed to the air for some time, because by the combined action of air and moisture, even when the material does not contain pyrites, a slow combustion takes place, whereby the combustibility of the material is greatly impaired. As already observed, from brown-coal paraffin and paraffin oils may be extracted

Pit-coal, or Coal.

Coal. Iron ores and coal are the most useful minerals, and the most important of all inorganic products of nature. Without coals the industry of the world as now existing would have been simply impossible. Coals supply heat and are a source of power; and cheap coal is a most important incentive to extensive industry.

Coals are the mummified and carbonised remnants of an ancient flora belonging to a former phase of existence of our globe; and they exist as a distinct geological formation, which extends in some localities over an area of several square miles. As regards the mode of formation of coal different opinions are current. The simplest view is that a peculiar kind of decay, aided by the internal heat of the earth, and modified by the pressure of superincumbent rocks and sedimentary deposits, has taken place among the plants, which have been gradually converted into a more or less pure carbon. Hence anthracite is a nearly pure carbon; while the different varieties of coal which contain bituminous and volatile matter are less completely decayed. The hydrogen and oxygen escape in combination with carbon as marsh-gas and carbonic acid and as petroleum. Anthracite must be viewed as the final product of the slow process of decay through which brown-coal and pit-coal pass.

	Carbon.	Hydrogen.	Oxygen.
Cellulose	52·65	5·25	42·10
Peat from Vulcaire	60·44	5·96	33·60
Lignite	66·96	5·27	27·76
Earthy brown-coal	74·20	5·89	19·90
Coal (secondary formation)	76·18	5·64	18·07
,, (coal ,,)	90·50	5·05	4·40
Anthracite	92·85	3·96	3·19

The most important explored coal deposits in Europe are:—In England:* The South Wales coal formation extending over an immense area; the Staffordshire and Yorkshire coal basins, the latter of which stretches to the Durham and Northumberland basins, and these again to those met with in the Southern parts of Scotland. 2. In Belgium: The basin of the Maas, near Liège, and those of the Sambre and of Mons. 3. In France: The basins of the Loire, of Valenciennes, of Creuzot and Blanzy, of Aubin, of Alais. 4. In Germany: The Silesian coal basin, those of the Saar, of the Ruhr, a tributary river of the Rhine, the basins near Zwickau and Plauen, &c. 5. In Austria: the Bohemian coal basin at Pilsen, and those of Brandau and Schlan. The largest of the European coal deposits or basins is very small compared with those situated in North America. The largest of the American deposits is that which stretches from near Lake Erie to the Tennessee river, through the states of Pennsylvania, Virginia, Kentucky, Tennessee, and known as the Apalachian coal field. The coal fields of Illinois and of Canada are not much smaller.

Accessory Constituents of Coal. Iron pyrites, or mundic, as the pitmen term it, is in the tesseral or in the rhombic shape, a very common accessory constituent of coal, which by being impregnated with this material may not only become unfit for use in certain operations, but is liable to crumble to dust, as is the case with many kinds of the Welsh coals which are thoroughly incorporated with pyrites, because the pyrites on coming into contact with air are oxidised and increase in bulk, forcing the coal asunder. This oxidation may become so active as to give rise to spontaneous combustion of the coal even in the seams. Galena, copper pyrites, and black-jack (native black sulphuret of zinc), also occur occasionally in coal. Among the earthy minerals, carbonate of lime, gypsum, heavy spar, clay, ironstone, and blackband (an iron ore), are frequently met with.

Classification of Coals. Abroad coals are classified with respect to their behaviour under combustion, as—1. Caking coals, which on having been reduced to powder and then ignited in a closed crucible to red heat, cake together. 2. Sintering coals, the powder of which agglutinates without fusing. 3. Sandy coals, the powder of which neither cakes nor agglutinates when ignited. In England coals are usually classified as—1. Gas coal. 2. Household coal. 3. Steam coal.

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* The yield of coals in great Britain is annually increasing, for in 1860 it amounted to 80 millions of tons; in 1868 to 104 millions; in 1869 to 108 millions; and in 1870 to 113 millions of tons.

Comparing the elementary composition of the coals with their chemical and physical properties, it appears that caking coals contain a bitumen consisting of carbon and hydrogen ready formed, or what is more likely formed at a high temperature. The larger quantity of oxygen present in sintering coals causes less bitumen to be formed; while in sandy coals a still smaller quantity of bitumen is formed. The most recent researches on coal disprove the opinion, that with an increase of the quantity of oxygen the caking should decrease, and that, consequently, the coals which contain the largest quantity of oxygen should be sandy coals. Coals exhibiting almost the same elementary composition behave very differently when exposed to heat.*

Anthracite. This carbonaceous mineral is to be considered as the final product of the process of decay which has converted plants into coal. Anthracite is found in the metamorphic rocks deposited in seams between clayey slate and greywacke, also between deposits of mica slate. Anthracite is amorphous and thereby distinguished from graphite; it is deep black coloured, brittle, exhibits a conchoidal uneven fracture, burns with a scarcely luminous flame, and without producing smoke. It does not become soft in the fire, but frequently decrepitates.

Jacquelain's analysis of several anthracites led to the following results:—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.
From Swansea	90·58	3·60	3·81	0·29	1·72
„ Sablé	87·22	2·49	1·08	2·31	6·90
„ Vizille	94·09	1·85	„	2·85	1·90
„ Isère Department, France ...	94·00	1·49	„	0·58	4·00

Anthracite is an excellent fuel for many purposes, and yields, especially with the blast, a very strong heat. It is therefore largely used in Wales in metallurgical operations, for burning lime and bricks, and in stoves for household purposes. In Pennsylvania, anthracite is met with and used largely in the reduction of iron ores.

Caking Coal. In addition to its behaviour under combustion, this coal is characterised by its deep black colour, ready inflammability, and by yielding when heated in closed vessels a compactly fused coke. Designating, with Fleck, the quantity per cent of carbon in ash-free coaly matter as C, the free hydrogen as W_1, the combined hydrogen as W, the oxygen and nitrogen as S; then $(C+(W+W_1)+S=100)$. W_1 is found by calculation on the supposition that 8 per cent oxygen holds in combination 1 per cent of hydrogen; consequently $W_1=\frac{S}{8}$; and this deducted from the total quantity of hydrogen, gives as difference the free hydrogen $=W$. The caking property of a coal is due to the proportion that upon 100 parts of carbon there should not be less than 4 of hydrogen. Caking-coals are especially suited for gas manufacture, though Fleck designates as such, in the widest sense, all coals containing upon 1000 parts of carbon at least 20 of combined hydrogen. But as the value of such a gas-coal depends upon the free hydrogen, which with carbon will yield volatile hydrocarbons, for the purpose of rendering the flame luminous, coal containing upon 100 parts of carbon 2 parts of combined (or fixed) and 4 of free or disposable hydrogen may be considered as the best gas coal and the strongest caking coal.

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* E. Richters has recently described a method for the comparative determination of different kinds of coal. See Dingler's Polyt. Journ., vol. 195, p. 72.

Because they contain a larger quantity of hydrogen than other kinds of coals, caking-coals are more readily inflammable and evolve the strongest flame. Strongly caking coals, however, are not well suited for use as fuel by themselves, owing to the fact that by the fusion, as it were, they undergo, they greatly impede access of air at the open fire-bars. Caking-coal is an excellent fuel on the forge-hearth, because by caking together it forms a receptacle for the blast from the bellows, and increases the heating effect. The peculiar kind of small coal used by blacksmiths is known in the French language as *charbon de forge*, *houille maréchale*, and is in England termed *smithy-coal.*

Sandy-coal is the poorest quality. It contains much oxygen, suffers great contraction when converted into coke, leaving a sandy, small coke. This kind of coal contains less than 4 per cent of free hydrogen; it is used as fuel for burning bricks, lime, and for similar purposes where a cheap fuel is required.

Sintering-coal exhibits an iron-grey colour, is frequently very lustrous, far less readily ignited than caking-coal, often contains much pyrites, and is employed where a strong and lasting heat is required. It is, therefore, used industrially on the large scale as a steam coal, as fuel for metallurgical purposes, &c. This kind of coal yields only a small quantity of gas, and when burnt for coke in coke-ovens it is scarcely changed in bulk, yielding a loose somewhat porous coke. 100 parts of the combustible portion of this coal contain less than 4 parts of free and less than 2 parts of combined hydrogen. Some kinds of anthracite belong to this class of coal; but the real anthracite is to be viewed as a native coke produced in a peculiar manner, not comparable with the process of coke-making as carried on industrially.

The physical properties of coal may be judged from the quantity of hydrogen contained, and we find that :—

Caking coals	contain upon	100 C.,	more than	4 W_1,	less than	2 W.
Gas and caking coals	,, ,,	100 C.,	,, ,,	4 W_1,	more than	2 W.
Gas and sandy coals	,, ,,	100 C.,	less than	4 W_1,	,, ,,	2 W.
Sintering coals	,, ,,	100 C.,	,, ,,	4 W_1,	less than	2 W.

Assuming coals to contain on an average 5 per cent of hygroscopic and 5 per cent of chemically combined water, the average composition is :—

Carbon	69—78
Hydrogen	3— 4
Chemically combined water and hygroscopic water	13—23
Ash...	3

The composition of the ash varies, greatly depending, not only as regards quality, but also the quantity of the constituents, upon a variety of causes, among which the geological age of the coal, the formation in which it is found, and others, have great influence. The ash consists chiefly of an alumino-silicate, or of gypsum and sulphuret of iron, mixed with larger or smaller quantities of lime, magnesia, carbonic acid, oxides of iron and manganese, with very small quantities of chlorine and iodine. Ash which contains much alumina and little silica is infusible. Ash containing much silica, but not any or only a small quantity of oxide of iron, sinters, but does not fuse; but ash which contains oxide of iron and alkaline silicates readily forms a slag, and may give rise to loss of fuel by enveloping the particles of coal. The quantity of ash found by incinerating coal in a small crucible varies from 0·5 to 20 and 30 per cent. By washing coals, small coal especially, a portion of the mineral matter may be eliminated.

Calorific Effect. The subjoined table exhibits for average coals the calorific effect, specific gravity, and composition:—

	Anthracite.	Caking coal.	Sintering coal.	Sandy Coal.
Composition:—				
Carbon	85	78	75	69
Hydrogen	3	4	4	3
Chemically combined water ...	2	8	11	18
Hygroscopic water	5	5	5	5
Ash	5	5	5	5
Calorific effect:—				
Absolute	0·96	0·93	0·89	0·72
Specific	1·44	1·17	1·16	1·06
Pyrometric	2350°	2300°	2250°	2100°
1 part reduces lead	26—33	23—31	19—27	21—31
1 part heats water from 0°—100 ...	60·5—74·7	52·87—2·0	44·06—1·6	50·0—71·0
Sp. gr.	1·41	1·13—1·26	1·13—1·30	2·05—1·34

It is assumed in practice that the heating effect of a good coal is very nearly that of wood-charcoal, and twice that of dry wood. In smelting operations the heating effect of coals is taken by bulk to that of wood by bulk as 5 : 1, and by weight as 15 : 8. According to Karsten's researches:—

100 parts by bulk of coal in the reverberatory furnace = 700 parts by bulk of wood.
100 „ by weight „ „ „ „ = 250 „ by weight of wood.

In boiling operations:—

100 volumes of coal = 400 volumes of wood = 400 volumes peat.
100 parts by weight of coal = 160 parts by weight of wood = 250 parts by weight of peat.

Evaporative Effect of Coals. This forms the most important industrial investigation which can be made with coals. In order to ascertain the evaporative effect, we must know—1. The quantity of hygroscopic water contained. 2. The quantity of ash or non-combustible matter it contains. 3. The composition of the organic matter.

As Hartig's experiments have proved that the evaporative effect of the organic matter of coal is the same for nearly all kinds of coal (= 8·04 to 8·30 kilos. of steam), the evaporative effect of any given sample of coal can be ascertained by estimating the quantity of water and ash it contains. According to W. Stein, the practical evaporative effect on the large scale may be taken as equal to two-thirds of that which has been calculated from the chemical composition of the coal. The practical evaporative effect of the coals in use in Southern Germany is, according to laboratory experiments and experiments made on the large scale, the following:—

			Ash.	Practical evaporative effect.
Ruhr coals,	I.	quality	5·00	7·20
Zwickau black pitch-coal,	I.	,,	6·06	6·45
,, ,, ,,	II.	,,	15·41	5·61
Bohemian coal,	I.	,,	6·60	5·80
,, ,,	II.	,,	6·90	4·90
,, ,,	III.	,,	10·30	4·20
Saar coal,			21·50	6·06
Stockheim coal,	I.	,,	6·30	2·72
,, ,,	II.	,,	8·40	3·86

The average evaporative effect of the Hartley steam coals is 14 lbs. of water for 1 lb. of coal.

Boghead Coal. This mineral, also known as Torbane Hill coal, found in the neighbourhood of Bathgate, a town situated between Edinburgh and Glasgow, belongs, with the blattel-coal of Bohemia, to a peculiar fossil fauna, and is especially suited for the manufacture of paraffin and oils, owing to the large quantity of bituminous matter it contains. Boghead coal is now solely employed in the preparation of paraffin and oils; and the supply, which is very limited, because the seam is almost exhausted, has been secured by Mr. Young, of Bathgate Works.

100 parts of Boghead coal contain:—

Carbon	60·9	65·3
Nitrogen	0·7	0·7
Hydrogen	9·1	9·1
Sulphur	0·3	0·1
Oxygen	4·3	5·4
Water	0·3	0·5
Ash	24·1	18·6

Boghead coal was formerly employed for gas-making, 1 ton yielding 15,000 cubic feet of a highly illuminating and very durable gas. Many varieties of the Scotch cannel-coals are suitable and are used for the preparation of paraffin and oils, and have therefore so greatly increased in price that these coals—the Wemyss, Rigside, and others—are now seldom employed for gas manufacture.

Petroleum as Fuel.

Petroleum as Fuel. Native, as well as artificially prepared petroleum, is, under certain conditions, a very valuable heating material. The sp. gr. of this oil varies, at 0°, from 0·786 to 0·923, while its coefficient of expansion for 1° varies from 0·00072 to 0·000868. The experiments as to the application of petroleum as fuel for marine purposes in America have proved that petroleum is three times more efficient than coal; and as the complete combustion of petroleum does not produce smoke, but simply evolves carbonic acid and watery vapour, a tall chimney is not required. Coals may be burned in marine boilers with the same effect, proved by a series of experiments made about fifteen years ago, on the large scale, by the late Dr. Richardson, of Newcastle-upon-Tyne, in conjunction with Messrs. J. A. Longridge and Sir William Armstrong. As petroleum contains 14 per cent of hydrogen, the condensation of the gases of combustion yields a large quantity of water which may serve for feeding the boilers, while the heat thus set free may be employed for the purpose of heating the feed-water. According to H. Deville, there is no difficulty in regulating the supply of petroleum, and it is not necessary to heat it previously. According to Fr. Storer, 1 kilo. of crude petroleum evaporates 10·36 kilos. of water, while 1 kilo. of anthracite coal evaporates only 5·1 kilos. of water. The theoretical evaporative effect of the purest petroleum is 18·06 kilos., as may be deduced from the percentage composition of petroleum, viz.:—

$$\begin{array}{llll} \mathrm{C} & \ldots\ 0{\cdot}86 & \ldots & 8080=6948 \\ \mathrm{H} & \ldots\ 0{\cdot}14 & \ldots & 34{,}462=\underline{4824} \\ & & & 11{,}772 \text{ units of heat; } \quad \frac{11{,}772}{652} = 18{\cdot}06 \text{ kilos.} \end{array}$$

The heating effect of different kinds of petroleum has been ascertained by H. Deville (1866—1869) to be as follows:—

Heavy oil from West Virginia	10,180	units of heat.	
Light oil from ,, ,, ...	10,223	,,	,,
Light oil from Pennsylvania	9,963	,,	,,
Heavy oil from Ohio	10,399	,,	,,
Oil from Java (Rembang)	10,831	,,	,,
Oil from Java (Cheribon)	9,593	,,	,,
Oil from Java (Soerabaya)	10,183	,,	,,
Petroleum from Schwabwiler (Alsace)...	10,458	,,	,,
Petroleum from East Galicia	10,005	,,	,,
Petroleum from West Galicia	10,235	,,	,,
Crude shale oil from Autun (France)...	9,950	,,	,,

More recently, R. Foote, Wyse, Field, Aydon, H. Deville, Dorsett, and Blyth, have constructed petroleum furnaces suitable for steam-boilers, which answer the purpose well. Petroleum lamps are used abroad, instead of spirit-lamps, for domestic purposes, viz., heating tea- and coffee-urns, tea-kettles, &c.

Coke.

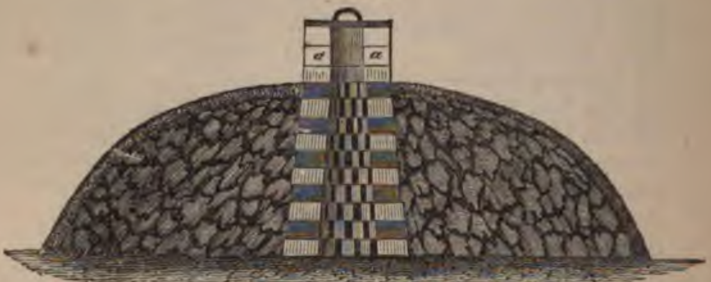
Coke. By coke we generally understand carbonised coal; and in England there is no other description of coke than oven- and gas-coke, referring of course to the mode of production.

Coke is prepared for the purposes:—1. Of increasing or rather concentrating the quantity of carbon in coal, and thus to obtain a fuel which will yield a more intense heat than coal. 2. For the purpose of converting coal into a fuel deprived of its volatile constituents, so as to obviate the unpleasant smell emitted by the combustion of coal when used to heat rooms in dwelling-houses. 3. For the purpose of converting coal into a fuel which does not become pasty when ignited, coal, in consequence of this property, being unsuitable for use in blast, cupola, and other furnaces. 4. For the purpose of eliminating from the coal a portion of the sulphur contained as pyrites. Before being converted into coke, coal, and especially small coal or coal mixed with slaty shale, fire-clay, and other heterogeneous mineral matter, is washed, as it is technically termed, the operation consisting in a process of purification by means of suitably constructed machinery, and the aid of a stream of water, the *rationale* of the process being that the mineral matter, which is about three times heavier than the coal, is deposited. The machinery in use for this purpose is similar in construction to that employed for washing metallic ores. By this method of purifying coal, the quantity of ash (mineral matter) it contains may be reduced from 10 or 12 to 4 or 5 per cent; but it should be borne in mind that 7 to 8 per cent of the coal is lost as dust. Bessemer has suggested the use of a solution of chloride of calcium, so concentrated that the coal may float on its surface, while the mineral matter will sink. The residues of coal-washing may contain so much iron pyrites as to be fit for use in the preparation of sulphuric acid (see p. 203).

The operation of coking is carried on in heaps, in ovens, or in retorts; but in the latter case the object is not so much to prepare coke as to obtain gas, tar, and other products from coal. The construction of coke-ovens according to Knab's plan, admits of obtaining from the coal, tar, ammoniacal water, and other volatile products.

Coking in Heaps. This method of converting coal into coke is very similar to that in use for converting wood into charcoal; but the central shaft, 1 to 1·5 metres in height, is in this instance made of fire-bricks, having a diameter of 0·3 metre, and provided with several lateral air-holes, Fig. 313, by means of which the mass of coals is brought in connexion with the central shaft. The largest lumps of coal are placed next to the shaft, being filled up with small coal, technically termed cinders and culm. At the bottom of the heap channels are constructed radiating towards the centre. The bottom of the shaft is filled with dry wood, which is kindled from the top. The opening at the top is not closed with the iron cover fitted to the shaft as long as any smoke from the smouldering coal is emitted. When no more smoke is emitted, the air-channels at the bottom of the heap are stopped with wet sand and coal-dust. In England the cooling of the glowing heap is hastened by pouring on cold water, whereby a greater degree of desulphuration of the coke is obtained.

FIG. 313.



Coking in Ovens. In the present day coal is converted into coke almost exclusively in ovens constructed for this purpose; because it has been found that by the use of ovens the operation is more readily conducted, while a larger quantity and a better quality of coke are obtained. As regards the construction of coke-ovens, some are so built that the gases and vapours evolved during the operation of coking, escape without being utilised. Others again are so arranged that the combustible gases are employed as fuel for coking the coal, or as fuel for steam-boilers or other purposes. This kind of oven is constructed with or without admission of air. To the latter class belongs Appolt's coke-oven, which is essentially similar to a vertical gas-retort, fitted with apertures for the exit of the evolved gaseous matter. Other coke-ovens again are so constructed that the tar and volatile products of the dry distillation of the coal may be condensed, collected, and utilised. Knab's coke-oven is thus arranged.

Among the coke-ovens of older construction is one, Fig. 314, in use at the Gleiwitz ironworks in Silesia. A is the body of the oven or kiln, with lateral openings, *o o o*, which can be closed by dampers or iron plugs; similar apertures are made in the bottom of the oven. The top of the kiln is vaulted, with the large opening, *b*, which serves, as well as the lateral doorway, *a*, for the introduction of the coals. The large lumps are placed at the bottom of the kiln, which is entirely filled, with the exception of a small space towards the top of the doorway, left for the purpose of throwing in ignited coals. The doorway, *a*, is bricked up, only a small channel being left for the introduction of the ignited coal. *f* is an iron pipe for carrying off the volatile products of the smouldering of the coals; *d* is an iron lid fitting tightly in the opening *b*. At the commencement of the operation all the openings of the oven, excepting those at *f* and those at the bottom, are closed; and as soon as there appears at the lower apertures an orange-coloured glow, these openings are closed, and those of the next row opened, and kept open for about ten hours; the third row of openings being then unplugged and kept open for sixteen hours; finally, the fourth row is opened for about three hours, after which the oven is left to cool—all openings being plugged—for twelve hours. The door, *t*, is then broken up, and the coke drawn from the oven by means of iron rakes. This description of oven contains 35 to 40 cwts. of coal, and the average yield of coke is 53 per cent by weight and 74 per cent by bulk. The gases and vapours issuing from *f* are carried to a condenser. 1 cwt. of coals yields 10 litres of tar.

The coking of small coal, culm, coal-dust, either previously washed or not, is carried on in ovens similar in construction to those used for bread-baking. Small coal, especially of the caking quality, yields excellent coke, and in many instances, this fuel is now guaranteed not to contain more than 6 per cent of ash. The mode of construction of coke ovens for small-coal coking differs in various countries. Fig. 315 exhibits a vertical section of such an oven in use by the Leipzig-Dresden Railway Company. The coking-room, *a*, is 3·3 metres high. The doorway, *d*, 1 metre high and wide, can be closed with an iron door, provided at the top with four air holes. The chimney stalk, *b*, is rather more than 1 metre high. At each side of the doorway an iron hook, *e*, is fixed, for the purpose of supporting the rakes used by the labourers when drawing the coke. In this description of oven 50 Dresden bushels[*] of small coal and coal-dust are converted into coke in seventy-two hours. The coke obtained is very compact; but if the oven be lightly filled, a more spongy coke is the result. Fig. 316 exhibits the construction of the coke-oven at the Zaukerode colliery, near Dresden. The bottom or hearth of the coking-kiln is of a circular shape slightly inclined towards the doorway. The width of the hearth

FIG. 314.

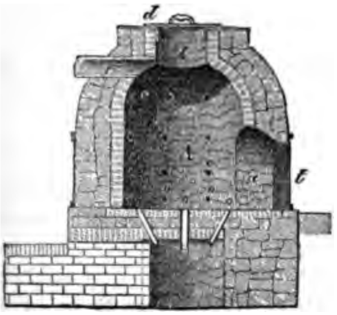
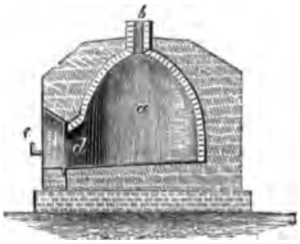


FIG. 315.



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[*] 1 Dresden bushel = 103·8 litres.

is 3·6 metres. The top of the vault *c* is 3·08 metres above the hearth. *b b* are two chimneys, each 1·3 metres in height, for carrying off the volatile product. The cast iron door is so arranged that at the top of the doorway an opening is left for the admission of air into the oven; *e* is a hook serving the purpose mentioned in the description of Fig. 314. Fig. 317 exhibits the vertical section, and Fig. 318 the ground plan of the coke-ovens in use at the collieries situated in the Saar district. The hearth of the kiln is egg-shaped, 3 metres long and 2 metres wide; while the height of the kiln is at most only 1 metre. The chimney, 1·75 metres high, also serves for the introduction of the coals. The admission of air to this oven is regulated by a channel at a height of 0·3 metre above the hearth; this channel, Fig. 318, communicates on both sides of the doorway, *t*, with the outer air, and communicates by means of the channels, *o o o*, with the interior of the oven. The door, *t*, fits rather tightly in the doorway. A quantity of 1 to 1·25 cubic metres (from 40 to 50 cubic feet) of small coal is converted into coke with this oven in 24 to 30 hours.

FIG. 316.

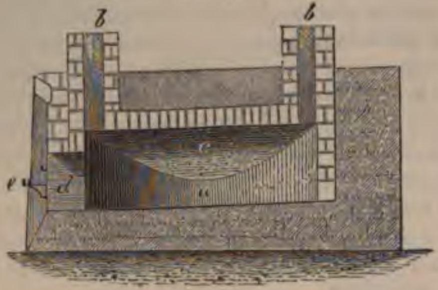
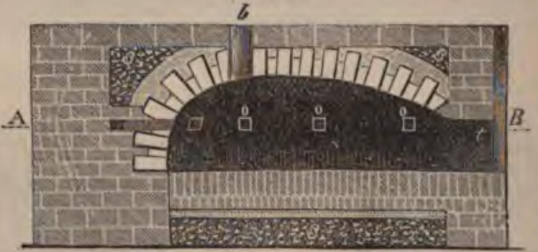
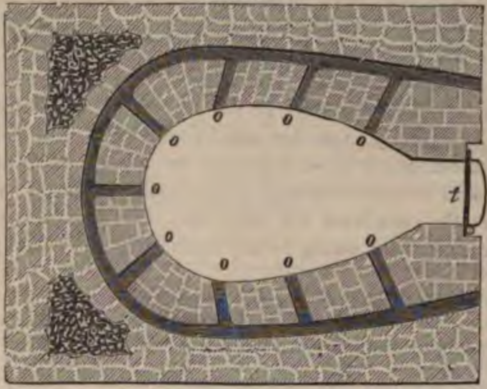


FIG. 317.



Among the coke-ovens constructed to utilise the escaping gases and heat for the purpose of making coke, that of Appolt deserves notice. The first of these ovens was built in 1855 at St. Avold. This coke-oven is distinguished from those described by its peculiar shape, which is that of a vertical shaft, heated externally, the heat being supplied by the ignition of the gases and vapours evolved from the coals while becoming coked. Fig. 319 exhibits a vertical section, and Fig. 320 a horizontal section of this oven. In order that the heat may reach the centres of the shafts, *a a*, their shape is that of a parallelogram, 0·45 by 1·2 metres, and 4 metres deep; 12 of such shafts form one oven. The separate shafts, the walls of which consist of hollow double walls, *b*, are connected with each other as well as with the lining walls, which forms a series of intercommunicating channels. Every compartment is provided with an upper and a lower aperture, through the former of which the coals are introduced, while through the latter—closed during the coking operation with an iron trap door—the coke is withdrawn. The apertures *e e* in the brickwork serve for the purpose of carrying off the gases and vapours which are burnt in the channels by the aid of the air rushing in at *ff*. The heat produced by this combustion converts the coals into coke. and the products of the combustion are carried off through the channels *g* and *h*. The dampers, R, serve to regulate the draught. The channels *g* communicate with the horizontal channel, *i*, the channels *h* with the channel *j*.

Fig. 318.



the channels *i* and *j* are carried into the chimney stalk, *k*. The compartments of the kiln, Fig. 319, are united at the top by a contraction of the brickwork, leaving to each only a small opening, closed by a cast-iron lid, fitted with an iron tube for the purpose of conveying a portion of the gases and volatile matter. On the top of the

Fig. 319.

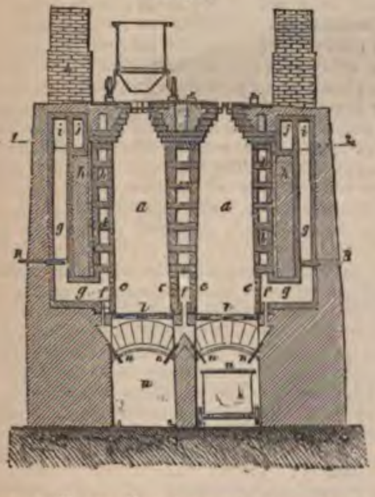
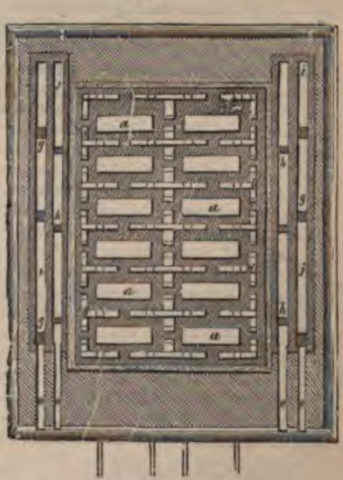


Fig. 320.



oven rails are placed, on which an iron truck runs, laden with the charge—25 cwts.—for each compartment. The coals are discharged into the compartments by opening a trap-door in the bottom of the truck. Under the vaulted brickwork, *u*, of the oven, trucks can be run for the purpose of being laden with the coke.

In order to set the oven in operation dry wood is thrown into the compartments, and this having been kindled, coals are thrown upon it. The interior of the oven soon becomes hot by the combustion of the gases issuing from the openings *e*. When the heat of the oven is sufficient to effect the decomposition of the coals and the combustion of the volatilised products, the compartments are charged, the iron lid being tightly luted to the top with clay. The charging is so conducted that the twelve compartments of the oven are filled in twenty-four hours, after which the coke in the first compartment is ready for being drawn, and fresh coal put in, an operation which is continued every second hour. As may be expected from the mode of construction, Appolt's coke-oven is rather expensive in the first building, the cost abroad being about £600, while an ordinary coke-oven may be built for £72 to £120; but Appolt's oven yields daily about 240 cwts. of coke—66 to 67 per cent from Duttweil coal, which in ordinary coke-ovens yields only 61 per cent. It should be mentioned, that with Appolt's ovens, the coke from the inner and outer compartments is not of the same quality and compactness, owing to the higher degree of heat prevailing in the former.

We may mention briefly the following contrivances for preparing coke, based upon the same principle as Appolt's. Marsilly's oven is covered with a brick arch, communicating with a flue through which the gases and vapours are carried under the hearth of the oven, and by burning there heat it. Jones's oven is similarly constructed, but with the difference that the combustion of the gases and vapours is made to take place in the coking kiln. This arrangement, used only with very dry, non-bituminous coals, certainly assists the coking process, because the air is heated previous to entering the kiln. Frommont's double cooking oven, in use on the Maas, in Belgium, as well as in Westphalia, and at Saarbrücken, is a stage oven, so constructed that the gases formed in the lower coking compartment are carried through channels to the upper hearth; thence with the gases formed in the upper compartment, are conveyed under the hearth of the lower oven, and thence through lateral channels to the chimney, so that the heat is thoroughly utilised. Gendebien's coking-oven is distinguished from that of Frommont, in so far that one of the upper coking compartments is placed over two of the lower; these ovens are chiefly used on the Sambre (Belgium). The coke-ovens according to Smet's plan are inclusive of the principles of all ovens built to utilise the heat of the combustible gases.

Dubochet's coking-oven, constructed in 1851 by Powell, is a tubular oven with sloping hearth, consisting of two shallow curved parts placed one above the other, and separated by doors. The upper part is the distillatory furnace or oven, the gases and vapours there evolved being conveyed under thè oven, and burnt with admission of air, the heat evolved by this combustion serving to coke the coals. The coke is caused to fall into a cooling oven, from which it is removed when extinguished. The combustible gases evolved by this process are sometimes employed for the purpose of heating a steam-boiler belonging to the coal-washing machinery. In the coke-oven built upon Knab's plan, the gases evolved from the coal are, previous to being burnt, deprived of the tar and ammoniacal water carried off by them. For this purpose the gases are conveyed to two large cylindrical vessels filled with coke, and in which nearly all the tar is deposited; thence the gases are conveyed to a system of tubes connected with water reservoirs for the purpose of eliminating the ammoniacal products. The purified gases are then conveyed to the furnace to be there burnt from a large circular burner, to the centre of which air is admitted. The necessary motion is imparted to the gases by bell-shaped exhausters, which draw the gases from the furnace through the purifying apparatus and force them to the burner. According to the statement of Gaultier de Claubry, there are 150 tons of coal converted daily into coke, in eighty-eight ovens belonging to the Société de Carbonisation de la Loire, near St. Etienne. The yield in 100 parts is:—

Coarse coke (large lumps) ..	70·00	Tar	4·00
Small coke	1·50	Ammoniacal water	9·00
Breeze	2·50	Gas	10·50
Graphite	0·50	Loss	1·92

It is questionable whether the coke thus obtained is equal in quality with that obtained by the ordinary coke-ovens; because experience proves that all coke prepared in close vessels, is rather porous and less suitable for use on locomotive engines and in blast-furnaces.

Very small coal and dust are converted into coke in ovens built similarly to those used for baking bread. The large quantities of refuse coal, screenings, &c., formerly waste, to be found in enormous heaps near coal-pits, and to effect their removal being frequently set on fire, burning for month after month, producing huge volumes of smoke, are now utilised and made into excellent coke, after having been first washed.

The coke drawn from the ovens is extinguished with water or under ash. The former plan, however, is most frequent, and has the advantage of giving to the coke a peculiar silvery gloss. There is, however, more than one objection to this mode of extinguishing coke, because in the first place the coke absorbs and retains some water, which as it has to be evaporated when the coke is burnt, absorbs a portion of the heat generated by the combustion. Secondly, the weight of the coke is increased, and may be increased fraudulently to a large extent, as some portions of the coke—the more porous lumps—take up 120 per cent of their weight of water, while the dense metallic portion takes up only 1½ per cent., and the coke from the bottom part of the oven 13 per cent. On an average the coke takes up by being extinguished by water 6 per cent of its weight; but cold coke takes up when thrown into water hardly half as much.

Properties of Coke. Well burnt coke or oven coke, is a hard, uniform, compact, solid mass, difficult to break, and not honeycombed, nor very porous. Its colour is black-grey or iron-grey, with a dull metallic gloss. Good coke should contain very little sulphur. All the sulphur contained in coal, chiefly as iron pyrites, cannot be completely eliminated by the coking process, as the sulphuret is only reduced to a lower degree of sulphuration. In the north of England it has been found, that if the coal, even when highly sulphurous, is first treated with a strong brine and powdered rock-salt, a coke very free from sulphur is obtained. The sulphur in coke is objectionable, from its action upon the ironwork of the furnaces, the fire-bars, &c.

Composition of Coke and its Value as Fuel. The average composition of good coke is the following:—

Carbon	85—92 per cent.
Ash	3— 5 ,,
Hygroscopic water	5—10 ,,

Owing to the great density and compact structure of coke, and the fact that it does not contain any combustible gases, it is ignited with difficulty, and requires for kindling a strong red heat, with a blast for continued burning.

According to a series of experiments in Prussian ironworks with coke in furnaces with hot blast:—

100 parts by weight of coke = 80 parts by weight of charcoal.
100 ,, bulk ,, = 250 ,, ,, ,,

Brix found that a coke made from upper Silesian coals, and containing 5·9 per cent of water and 2·5 per cent of ash, yielded for every kilo. burnt 7·15 kilos. steam.

Artificial Fuel.

Artificial Fuel. Under this name we understand an originally pulverulent, combustible fuel, such as small coal or coke, breese, sawdust, refuse wood, &c., mixed with tar or thin clay liquor, and by strong pressure subsequently moulded in the shape of bricks. Compressed peat and compressed spent tan are in a certain sense artificial fuel.

Peras. Under this name is known an artificial fuel first prepared from caking coal by Marsais, the viewer and manager of some collieries near St. Etienne. The small coal, screenings, dust, and other refuse, are first lixiviated for the purpose of removing mineral impurities, such as gangue, clay, pyrites, &c. The purified coal is drained, then ground to powder by suitably constructed mill-work, afterwards dried by the application of heat, then mixed with 7 to 8 per cent of thick coal-tar, and finally moulded into bricks by the aid of strong pressure, the brick-shaped lumps weighing each about 20 lbs. Peras is less fragile than ordinary coal, and being of a uniform shape, can be better stored than coal, taking up about one-fifth less room, a matter of considerable advantage on board steamers. Similar to peras are the patent coals made by Wylam and Warlich.

The so-called moulded charcoal, or Parisian coal, introduced about fifteen years ago by Popelin-Ducarré, is an artificial fuel composed of charcoal refuse with coal-tar. The small lumps and dust of charcoal are mixed with 8 to 12 per cent of water, then ground to powder, and to 100 kilos. of the powder are added 33 to 40 litres of coal-tar. This magma is thoroughly incorporated and next moulded into cylinders. These are dried, and finally carbonised in a muffle-furnace. This fuel is far less fragile than ordinary charcoal, better fitted for transport, burns better than coke, and even when only slightly kindled, continues to burn in air, which is not the case with coke.

Briquettes. When strongly caking coal is heated in closed vessels to 260° to 400°, and then compressed in moulds, the result is the formation of a hard brick-shaped fuel, very suitable for domestic use as well as for steam production.[*] It has been found that the manufacture of briquettes can be advantageously combined with the preparation of tar for the purpose of extracting benzol, carbolic acid, naphthaline, asphalte, and anthracen.

Gaseous Fuel.

Gaseous Fuel. The utilisation of certain combustible gases and mixtures of these gases as fuel has been practically solved only during the last few years, although in metallurgical operations the idea of such utilisation is of more remote date. The combustible gases used on the large scale as fuel are those evolved from blast-furnaces, and from coke-ovens and other apparatus in which these combustible gases are formed as the by-product of industrial operations. The composition of the blast-furnace gases varies of necessity according to the kind of fuel used, the temperature of the furnace, the shape, build, and height of the latter, the pressure on the blast, &c. The combustible gases escaping from these furnaces consist chiefly of carbonic oxide, hydrocarbons, hydrogen, carbonic acid, nitrogen, and of ammonia where coal or coke is used as fuel. The so-called generator gases are those combustible gases which are evolved from solid fuel, coke, peat, or wood, by its carbonisation in a separated furnace, kiln, or oven, with or without the aid of a blast. These combustible gases may be utilised in various ways and obtained from fuel which is not otherwise applicable as such. According to Ebelmen these gases are composed as follows:—

	Generator gases obtained from:—			
	Wood-charcoal.	Wood.	Peat.	Coke.
Nitrogen	64·9	53·2	63·1	64·8
Carbonic acid	0·8	11·6	14·0	1·3
Carbonic oxide ...	34·1	34·5	22·4	33·8
Hydrogen	0·2	0·7	0·5	0·1

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[*] See Th. Oppler, "Die Fabrikation der künstlichen Brennstoffe, insbesondere der gepressten Kohlenziegel oder Briquettes," Berlin, 1864; also "Jahresbericht der chem. Technologie," 1864, p. 760; 1866, p. 333; 1868, p. 800.

There has long been in use in England a gas mixture obtained by passing high-pressure steam over red-hot coke contained in retorts. Siemens's regenerative gas-furnace, described on pp. 24 and 273, belongs to this category. Combustible gaseous bodies are largely utilised in metallurgical operations, puddling-furnaces, zinc-smelting, &c.

Gas for Heating Purposes. It has of late years been frequently suggested that a cheap gas should be manufactured for heating purposes. In Berlin a company has been formed under the technical guidance of C. Westphal and A. Pütsch, the object being to prepare gas from brown-coal at Fürstenwald, a distance of about 38 kilometres from the city. The intention is to construct twelve retort-houses, each to contain seventy furnaces provided with ten retorts, to be fired as in Siemens's regenerative gas-furnace. The purified gas is to be forced by blowing-machines, actuated by steam-engines of 360 nominal or 500 indicated horse power, into a main pipe of 1·3 metres diameter constructed of boiler-plates and carried above ground supported on iron pillars. The gas will be collected at Berlin in twelve gas-holders, each of 750,000 cubic feet capacity. The pressure of the gas in the mains and service-pipes within the city will be 1·5 centims. water-gauge, in order that pipes of smaller diameter may be used. According to Ziureck, the composition of the gas obtainable from the brown-coal is, at a sp. gr. of 0·5451, as follows:—

Hydrogen	42·36	per cent.
Carbonic oxide	40·00	„ „
Marsh gas	11·37	„ „
Nitrogen	3·17	„ „
Carbonic acid	2·01	„ „
Condensable hydrocarbons	1·09	„ „

A gas of this composition will answer admirably for heating purposes. 3000 cubic feet of it are in heating effect equal to 1 ton of brown-coal, and equal to ⅓ ton of pit-coal, the ton being equal in this case to 275 to 300 lbs. The price will be 7½d. per 1000 cubic feet, so that the heating effect yielded by it as compared with the price of a ton of coals will be about 4s. 6d. The works are constructed for an annual production of 9500 millions of cubic feet of gas, or a daily supply of 2⅔ millions of cubic feet.

Heating Apparatus.[*]

Warming. We understand by warming the heating of any room or space by heat evolved from the combustion of fuel. The room or space may be an apartment in a dwelling-house, a church, a steam-boiler, a glass-house, a hothouse in a botanical garden, &c. It is the aim of technology to apply the fuel so as to yield by its most economical use the greatest amount of heat. In order to obtain by the combustion of fuel as nearly as possible its absolute and specific calorific effect, the combustion should not only be complete, but the gaseous products should suffer the highest degree of oxidation; in other words, neither smoke nor any combustible gases

[*] The following works afford very valuable information on this subject:—C. Schinz, "Die Wärme Messkunst," Stuttgart, 1858; E. Péclet, "Traite de la Chaleur," 3rd edition, Paris, 1861-62, 3 vols; and for stoves for domestic use, "Die Badische Gewerbezeitung," edited by H. Meidinger.

should be evolved. The practical importance of this principle is exhibited by the following:—

1 part of carbon yields, when burnt to carbonic oxide, 2480 units of heat.
1 ,, ,, ,, ,, ,, carbonic acid, 8080 ,, ,,

In order to obtain complete combustion, the fuel should be supplied with the requisite quantity of air, while the vitiated air should be carried off with the gaseous products of the combustion. This supply of air or draught can be assisted artificially by means of blast- or exhaust-apparatus; but in most cases the draught is natural, *i.e.*, produced by the calefaction of the air, which becoming specifically lighter, ascends.

All heating apparatus consist of three distinct parts—the fire-place or hearth, the heating-room, and the chimney. The hearth is that portion where combustion takes place. The heating-room is the portion of the apparatus where the heat generated is utilised, and the chimney is a channel, usually placed in a vertical position, and often connected by means of flues with the heating-room and hearth—through which the gases evolved by the combustion of the fuel are carried off, and a draught created maintaining an efficient combustion of the fuel.

The hearth or fire-place may vary greatly in shape and mode of construction. The most primitive, but also the most defective kind of hearth, is that on which the fuel, usually wood or peat, is placed on tiles or bricks under the chimney. Such arrangements are still in use in many remote country places, especially in the country districts of Ireland and Scotland, where faggots of wood and peat are thus burnt. In this manner a very great amount of heat is wasted and the supply of air not properly regulated; there is an excess of air supplied, and hence loss of fuel. The air required for the complete combustion of the fuel should be made to pass through the fuel, which for that purpose is placed on a grating, consisting of bars of iron or fire-brick. The space under the fire-bars is called the ash-pit, through which the air is supplied to the fuel. The hearth is usually provided with iron-doors, which are opened when fresh fuel has to be introduced. This plan is accompanied with the objection, that during the period of feeding and raking up the fire, a large quantity of cold air enters the hearth, and causes the combustion to become irregular and much smoke to be produced. The use of the so-called stage fire-bars, placed in the manner of steps, one above the other, is not attended with this defect.

When the fuel contains much sulphur, the iron fire-bars are soon worn out, owing to the formation of sulphuret of iron; in order to prevent this, it is often usual to leave a layer of clinkers and slag on the bars for the purpose of protecting them from the direct action of the fuel. In order to regulate the draught, dampers or similar contrivances are fitted to the flues, chimney, or funnel.

a. Heating Dwelling Houses.

Heating Dwelling Houses. The heating of dwelling-houses and public buildings, halls, theatres, churches, &c. (in connection with the ventilation), can be effected in various ways, either by radiant or conducted heat. According to the construction of the heating apparatus, we distinguish:—1. Heating by flues. 2. By stoves, or with hot air. 3. Air heating. 4. By means of steam or hot-air pipes. 5. Hot-water heating. 6. Heating by means of gas.

Direct Heating. The direct heating of rooms by the combustion of wood and other fuel on an open hearth, or in chaufing-dishes and small stoves without chimneys, is undoubtedly the most ancient and primitive method of heating. In the centre of the huts in Ireland and the Highlands of Scotland, a rough hearth is constructed, while the smoke evolved by the fuel escapes through a hole in the roof. In some parts of France, Italy, Spain, and Turkey, rooms are heated by means of a chaufing-dish containing burning charcoal, by the combustion of which the air of the room is vitiated, becoming unfit to be respired by the lungs. It is evident that for this reason and owing to the risks of fire this mode of heating is very dangerous.

Chimney Heating. This mode of heating, in general use in England and the larger towns of Scotland, Ireland, and Wales, is of ancient use, and is based upon the heating of the air of the rooms by the direct radiation of the heat of the fire. It is undoubtedly the most imperfect and wasteful method, as there flows into the chimney a very large excess of air above that required for maintaining the combustion of the fuel, the consequence being that strong draughts of cold air are felt near the windows and doors of the rooms, while a downward current of air is frequently created, causing the chimney to smoke. This mode of heating only suits countries enjoying an average mild climate and possessed of plenty of fuel. It would appear that among the reasons why this mode of heating is continued is the pleasure of seeing the fire and of warming the feet by it, notwithstanding that the other parts of the body remain comparatively cool. The arrangements of the method of warming by the radiant heat from chimneys are in the most primitive form the following:—At the lower part of the wall from which the chimney is built, a niche or recess is constructed in which the fuel burns; but in grates of better construction, the recess is not very deep, and less contracted where it issues in the chimney, while frequently the hearth is fitted with a sliding door, and a valve or trap-door in the upper part of the flue leading into the chimney.

In order to utilise a portion of the conducted heat, yet still to leave the heating to be effected chiefly by radiation, the flow of hot air into the chimney is to some extent intercepted, so as to form a combination of the methods of stove- and chimney-heating.

Stove Heating. This method of heating is in general use in the colder parts of the Continent, in America, Canada, &c. A well constructed stove should not consume too much fuel, the combustion of which should be complete, while the heat generated should be uniformly radiated, and only a very small quantity allowed to escape into the chimney. As a stove is placed at some distance from the chimney, the radiating as well as the conducted heat is utilised. The loss of heat is prevented by a series of flues; but in order to keep up a sufficient draught, the air escaping into the chimney should have a temperature of at least 75°. The fuel is generally introduced into the stove from the room, although some kinds of stoves are so constructed that they may be fed with fuel from the outside of the house similarly to the hot-house stoves; this method of construction entails a larger consumption of fuel and some loss of heat.

Stoves are made of cast-iron, sheet-iron, and fire-clay. Iron readily absorbs heat, and as the sides of the stove are usually not very thick, the heat is rapidly and readily dispersed. As iron stoves may become red-hot, the air surrounding the stove is chemically changed in consequence of the permeability of red-hot iron to carbonic oxide. This gas, according to the experiments of Deville and Troost, 1868, is absorbed and evolved by red-hot iron to 0·0007 to 0·0013 its volume. Fire-clay stoves yield a very uniform heat, given off only slowly and gradually.

Compound stoves are those in which the hearth is made of cast-iron, on which is placed a sheet-iron column closed at the top, and provided with a lateral opening communicating by sheet-iron pipe with the chimney.

We distinguish according to the material of which stoves are constructed:—

a. Those simply of iron.
b. Those of fire-clay.
c. Compound stoves.

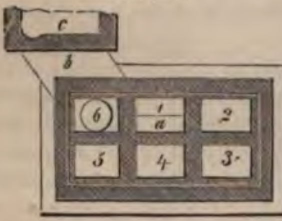
Iron stoves are usually so constructed that the heat generated by the combustion of the fuel is rapidly communicated to the air of the room. The heat generated in fire-clay stoves is communicated to the great mass of fire-clay of which the stoves are constructed, so that even long after the fire has been extinguished the stove continues to give off heat; these stoves are especially used in Sweden and Russia.

Iron Stoves. The construction of these stoves varies greatly. When made of cast-iron the shape is frequently cylindrical, a short pipe being cast on, to which is fitted a sheet-iron pipe leading to the chimney. In some cases the length of this pipe is considerable, in order that the heat evolved by the combustion of the fuel may be better utilised.

Sometimes iron stoves are constructed with an outer mantle which is perforated and usually exhibits an ornamental appearance; this mantle is placed at some few inches distance from the inner stove, in which the combustion of the fuel takes place.

Fire-clay Stoves. These stoves, made of a peculiar kind of clay, are externally glazed similarly to the so-called Dutch tiles. The construction of these stoves is very massive. They consist of a series of channels made of burnt clay and put together with a mixture of the same clay unburnt and gypsum. The thickness of the pipes forming the channels is 7 inches. The number of channels or flues is four to six, or even twelve. The Russian stove, Fig. 321 in ground plan, is fitted with six flues. Fig. 322 is a front, Fig. 323 a side view, and Fig. 324 a vertical section. *a* is the vaulted fire-place, the flame and smoke evolved by the combustion of the fuel being carried upwards in flue 1, downwards in flue 2, again upwards in flue 3, again downwards in flue 4, again upwards in flue 5, and again downwards in flue 6, and thence into the chimney by means of an iron pipe fitted to the stove.

FIG. 321.



Each of these stoves has a separate chimney, a tube 18 to 30 centimetres wide, carried straight up to above the roof of the house. These narrow chimneys, also in use in Edinburgh, Glasgow, and other Scotch towns, are constructed of fire-clay tubes fitted into the stone of the walls. As a Russian stove is really intended to be a store of heat, it has to be hermetically closed as soon as the fire is extinguished; this is effected by the following contrivance, termed in the Russian language, *Wiuschke*. Near the junction of the last flue and the stove-pipe a plate of cast-iron, Figs. 325, 326, and 327, is fitted to the stove, the plate being provided in the centre with an opening of 21 to 24 centimetres diameter. This opening has an internal vertical flange or collar of 2 centimetres, and an external vertical flange of 3 centimetres height. An iron cover, *a*, Fig. 327, fits closely on to the inner flange, and a larger cover, *b*, fits on to the outer flange, thus securing a tight joint. These ovens are heated with wood, which is sawn into small blocks. 'No smoke is evolved, because the high temperature prevailing in the flues consumes the smoke completely, and the wood is not used until it is thoroughly dry. The Swedish stove is usually cylindrical in shape, and very tall, reaching nearly to the ceiling of the rooms. The flues (four in number) of these stoves are of rather complicated construction. They communicate laterally with each other. The chimney pipe is placed at the top and is provided with a damper, closed when the fire is extinguished. The fuel, dry wood, required for one heating of the stove, is put into the stove at one charge, and when the combustion has ceased, the damper and the stove door are tightly closed.

Compound Stoves. Feilner has constructed a stove of this description, Figs. 328 to 331, which is a modification of the Russian stove. Fig. 328 shows a front view, and Figs. 329 and 330 vertical sections. The section exhibited in Fig. 329 is through the ground plan, Fig. 331, as indicated by the dotted line A A. The section shown in Fig. 330 is according to the dotted line B B and the section exhibited in Fig. 331 to the line C C. The hearth of this stove is constructed of iron surrounded by a burnt clay mantle or box. The products of

Fig. 322.

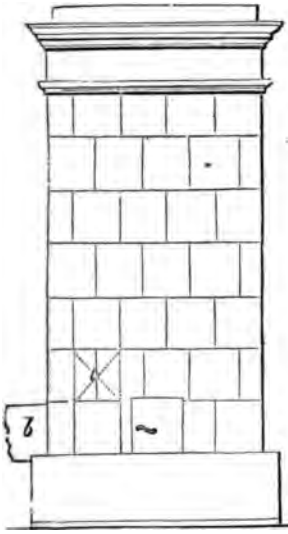


Fig. 323.

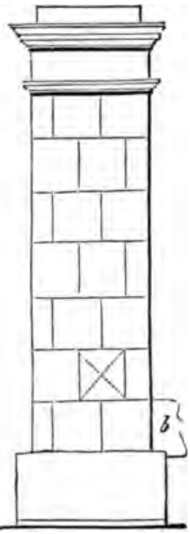


Fig. 324.

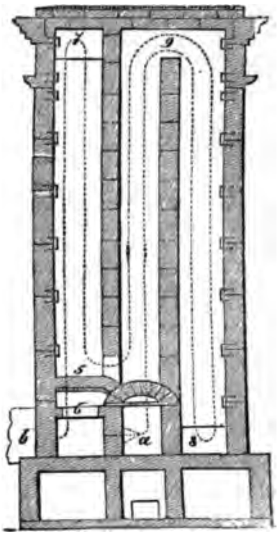


Fig. 325.

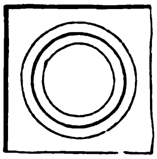


Fig. 326.

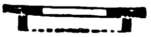


Fig. 327.

Fig. 328.

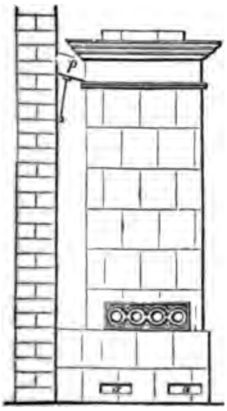


Fig. 329.

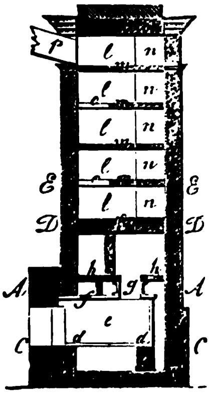
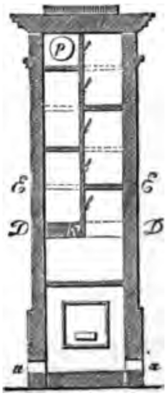
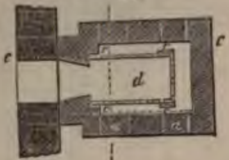


Fig. 330.



the combustion are forced through a cylindrical tube, of 12 to 18 centims. width, and thence issue into the flues. The combustion is very complete, no soot or smoke being formed.

Fig. 331.



This stove is divided into two compartments by means of a vertical wall; and horizontal shelves are fitted to this wall, thus forming a series of channels or flues, through which the products of combustion are made to pass. The length of these flues varies, according to the size of the stove, from 9 to 20 metres. As the hearth is so placed as to be a separate part of the stove, the room becomes heated as soon as the fire is lighted. In the lower part of the stove a kind of air-heating is arranged, because by two openings, *a a*, Fig. 328, cold air enters and becomes strongly heated while passing through the stove. When the combustion of the fuel has ceased the damper in the pipe leading to the chimney is closed; the clay portion of the stove having then been so strongly heated that one firing answers for a whole day. *b b b* is the brick-work foot of the stove; *c c* are supports for carrying the cast-iron bed-plate, *d d*, of the iron hearth; *e* are the side plates; *f f* the top plate of the fire-room; *g* is a tube fitted to the top plate, and intended for carrying off the gases and other products of the combustion of the fuel. On the top plate are placed fire-bricks supporting *h h*, which is made of boiler-plate, and provided with a circular hole so situated as to be free from the tube *g*. On this boiler-plate are roofing tiles, which reach to the side walls of the stove, and are covered with sand or dry ash. This construction is necessary for the purpose of preventing the iron hearth in its expansion forcing asunder the brickwork.

The vertical partition wall, *i*, is built of brick; it supports *k*. *l l* are also built of brick. *n n* are so short that each of the openings is 7 inches distant from the opposite side. The smoke is carried upwards through the openings *o o*. *p p* is the iron pipe, which communicates with the chimney. The heat and gases generated by the combustion of fuel in this stove proceed from the hearth, *e*, through *g*, are returned by *k*, flow along *i*, pass through the opening *o* into the flue *n*, and finally into the pipe, which communicates with the open air.

Henschel's stove, constructed to burn brown-coal, deserves notice. Fig. 332 exhibits a vertical section, and Fig. 333 a horizontal section at the line A B. This stove consists of

Fig. 332.

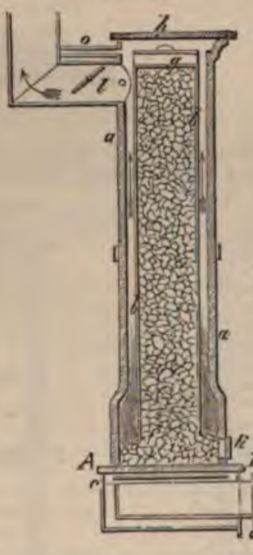
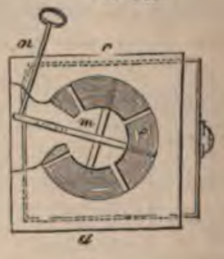


Fig. 333.



two iron cylinders, the outer, *a*, being of cast-iron, the inner, *b*, of stout sheet-iron The outer cylinder is supported by the ash-pit, *c d*, fitted with fire-bars towards the upper end. The inner iron cylinder does not reach to the fire-bars, and is closed at the top by a tightly-fitting cover, *g*, while the outer cylinder is closed by the lid *h*. When it is intended to heat this stove it is first filled with brown-coal, thrown in from the top after removal of the lids. The fuel is kindled at *i*, through *k*. The combustion can only take place on the fire-bars, the hot air flowing upwards between the two cylinders, and thence into *l*, the iron pipe leading to the chimney. The fuel contained in the inner cylinder gradually sinks downwards as the combustion proceeds. The ash is removed by imparting motion to the crossed iron bars, *m*, Fig. 333, to which are fitted pieces of iron passing between the fire-bars. The handle, *n*, projects outside the stove. Any smoke which might reach the upper part of the stove is carried off by the pipe *o*. This kind of stove having once been filled with fuel continues to supply heat for forty-eight hours. Meidinger, of Carlsruhe, has constructed many very excellent stoves of this description.

Air Heating. This method of heating is effected by means of stoves, but is distinguished from the ordinary stove-heating by the situation of the stove, which is in most cases not placed within the space or room to be heated, being within a chamber from which the heated air is conveyed by channels to the space intended to be warmed. The aim of air heating or central heating is to heat a large space uniformly with one stove, or to heat by means of one fireplace all the rooms and apartments in the same building, when it is not found convenient to construct fireplaces in each apartment. There are in use three modes of air heating, which differ from each other in the method of ventilating the space to be heated.

(*a*.) The cold air enters the heating apparatus, becomes warm, and is conveyed through a pipe or channel into the room or space to be heated, while an equal bulk of vitiated air escapes from the imperfectly-closed windows and doors.

(*b*.) The heated air is returned to the heating apparatus, becomes again warmed, and re-enters the room. While the method (*a*) has the advantage of constantly supplying fresh air to the room, thus creating an uninterrupted ventilation, the method (*b*) has the advantage of saving that quantity of heat which is lost in the efflux of warm air in the first method.

(*c*.) The outer air becomes heated at the fireplace, and is then conveyed to the room to be warmed. The vitiated air from the room is conveyed through a flue to the fire, this air serving the purpose of maintaining the combustion. This method combines all the advantages of (*a*) and (*b*), while, with constant ventilation, a saving of fuel is effected.

As regards the methods of employing air heating, we distinguish according to the construction of the apparatus:—

(*a*.) Air heating by means of a mantle oven.

(*b*.) Air heating by means of a heating chamber.

The first method is very similar to ordinary stove-heating, and only distinguished from it in the respect that the stove is surrounded by an outer mantle of bricks or fire-clay slabs, some 6 to 8 inches from the stove. This mantle is provided with openings, through which the heated air escapes, and is uniformly distributed through the room.

In warming with a separate chamber we have to consider the form of the chamber, a small vaulted room, built of brickwork, and containing the furnace. The heating chamber should be comparatively very small, so that the heated air shall be carried as rapidly as possible to the room intended to be warmed. The channels for carrying off the heated air are placed at the top of the heating chamber, while the channels for conveying the cold air are situated at the bottom. The space between the furnace and the walls of the heating chamber measures from 12 to 16 centims., but the vault is elevated 1 to 1·3 metres above the top of the furnace.

The furnace or stove is the most essential part of this air-heating apparatus. It is made either of cast-iron or of boiler plate; and as regards size 1 square foot of heating surface is capable of heating 800 to 1000 cubic feet of air. Another kind of air-heating apparatus consists of the following arrangement:—A series of rows of cast-iron tubes, which communicate, are so placed in a furnace or oven that cold air enters into the lowest row of the series, while the heated air escapes from the upper row. Since the hot air having become specifically lighter always tends to rise, it is clear that the apparatus should be placed in the cellar or lowest room of the building to be heated. The hot-air pipes should be as vertical as possible.

The apertures through which the hot air gains admission to the rooms to be heated are best situate in the floor, in this case generally a double one; or the hot-air pipes are placed in channels covered with an iron grating, and sometimes provided with a damper so that the supply can be regulated.

Heating with hot air is usually attended with a serious defect, viz., that the air is exceedingly dry or even burnt. This defect can be remedied only by supplying air with aqueous vapour by placing in the current of hot air shallow basins filled with water, or by suspending wet sponges near the pipes. Dr. von Pettenkofer has, however, proved that these expedients do not quite answer the purpose. Air heating is not very suitable for dwelling-houses, but answers best for public buildings, which, as churches, theatres, and concert rooms, require to be only occasionally heated, the defect of the too great dryness of the air being in these instances counterbalanced by the watery vapour exhaled in the process of respiration by the persons assembled, and by the gas lights.

Caloriferes. A system of air-heating by means of so-called calorifères has become rather general in the United Kingdom, North America, Sweden, Russia, Holland, Belgium, and also to some extent in Germany. It is usually employed in large buildings, but is also applicable to dwelling houses. Among the best of this kind of heating apparatus are those supplied by the London Warming and Ventilating Company, who employ the modification of a plan successfully introduced by Sir Goldsworthy Gurney in both houses of Parliament. Steam, hot water, gas, and coal or coke, in open or enclosed fire-places, are equally available for the process, while the cost is less and the effect greater than with any other known means. The apparatus are successfully in use in St. Paul's Cathedral, York Minster, eighteen other cathedrals, 1000 churches in England, and a large number of government, public, and private buildings, and mansions. Abroad, Hartmann at Augsburg, Boyer and Co. at Ludwigshafen, Bacon and Perkins at Hamburg, have invented more or less excellent calorifères. Those by Reinhardt and Sammet, at Mannheim, appear to be of very great efficacy; they are so contrived that the fuel is thoroughly burnt, not even any soot or smoke being left, while the air is rendered agreeably moist by the gentle dripping of water on the hot-air gulls. The temperature of the air can be kept uniform for days and weeks consecutively. As this apparatus if used in a dwelling-house is placed in the cellar and the whole house heated, there is no dust nor other inconvenience attending the ordinary fire-places. This apparatus consumes only a small quantity of fuel, and requires as an attendant an ordinary labourer. In the air-heating apparatus invented by Boyer and Co., Ludwigshafen, now in use in many large buildings in Münich, Würzburg, and other Bavarian towns, the heating pipes are not made of wrought-iron but of charcoal cast-iron, while the dimensions and shape are so arranged as to expose the pipes as little as possible to injury from the fire, and yet to afford a large heating surface. For every kilo. of coals hourly burnt, 2·5 square metres of heating surface are present. In order thoroughly to utilise the heat of the products of combustion, these products are caused to pass through a series of pipes, some of which are coated with a smooth layer of mortar, for the purpose of preventing loss of heat by radiation. The heat of the products of combustion escaping into the chimney is below 100°; and these products consist only of watery vapour and carbonic acid. In order to render the hot air supplied by this apparatus pleasantly moist, water is evaporated with the heated air at the rate of 1·5 to 2 litres per 100 cubic metres heating surface.

Flue Heating. This mode of heating, now confined to hothouses for plants, and even there superseded by better methods, consists chiefly in carrying the products of combustion of a stove or furnace through a series of pipes which are placed within the room to be heated, and are at the opposite end to the furnace connected with a chimney. If this plan is adopted for heating dwelling-houses, the furnace is placed in the cellar; but experience has shown that this method of heating, except in the case of hothouses, is too crude, and, moreover, dangerous, as by overheating of the flues fire may ensue.

Hot-water Heating. Instead of heating air directly, it is often heated intermediately by water, which, owing to its high specific heat, is eminently adapted to this purpose. This kind of heating is known as hot-water heating. 1 kilo. of water at 100° emits, while cooling to 20°, 80 units of heat, capable of heating 32 kilos., or 24·61 cubic metres of air to 10°. The system of hot-water heating is based upon the placing of a vessel filled with hot water in the space to be heated, care being taken to keep up the temperature of the water. In the ordinary hot-water apparatus, the fluid is never heated higher than its boiling-point, and is usually kept many degrees below that temperature; hence this method is termed low-pressure water heating.

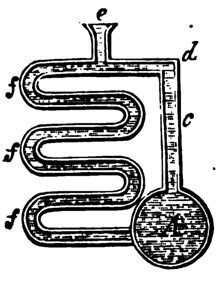
This low-pressure or ordinary hot-water heating is maintained—

a. By circulation through a closed boiler which is heated.

b. By circulation and syphon action between an open and a heated vessel.

a. In this method there is fitted to a boiler, quite closed, a series of pipes, through which the hot water is conveyed from and the cooled water returned to the boiler. The principle of the circulation of the water may be elucidated by Fig. 334. The water is heated in A, *c* is the ascending tube, *df* are the tubes through which the water is returned to the boiler. The tube *e* serves for the purpose of filling the apparatus with fresh water, as well as for the escape of any air or steam which might be evolved. The hot water ascending in *c* causes a circulation in the apparatus, which when once commenced is maintained as long as the heating is continued. From time to time it is necessary to unscrew the cap at *e*, for the purpose of adding a small quantity of water. Usually *e* is provided with a stop-cock, which admits of the introduction of a funnel. For 100 cubic feet of space to be heated, 20 to 30 square feet of heating surface are required. The heat of the warm-water apparatus is imparted to the rooms through stoves, usually made of sheet-iron. These stoves are cylindrical in shape, 2 to 3 metres high, by 0·3 to 0·7 metre diameter, and fitted with a series of pipes in which the air becomes heated by a larger hot-water tube.

FIG. 334.



b. The other method of hot-water heating by means of an open boiler with syphon action, or the so-called thermo-syphon of Fowler, as compared with the first method, has the disadvantage that from an open boiler a considerable loss of heat is unavoidable, while it is difficult also to prevent accumulation of air on the upper part of the syphon tube. The height to which the tubing can be carried is in this system, too, limited to the height equivalent to the atmospheric pressure, about 30 feet for a column of water.

Perkins's so-called high-pressure hot water system, wherein the temperature of the water in immediate contact with the fire is raised to 150°, 200°, and even 500°, consists of a closed tube filled with water. One-sixth of the length of this tube is coiled and placed in a furnace; the other five-sixths are heated by the circulation of the hot water. The tubes are of malleable iron, capable of resisting a pressure of 3000 lbs. per square inch. More recently the hot water from native hot springs, or obtained from bored artesian wells, has been, as for instance at Baden-Baden, employed for the purpose of heating. At Baden-Baden the hot water (67°) from a native spring is used to heat a church.

Heating with Steam. This method of heating is based upon the latent heat contained in steam. 1 kilo. of steam at 100° contains so much latent heat that by it 5·5 kilos. of water can be heated from 0° to 100°.

A steam-heating apparatus consists of a boiler, steam-pipes, and pipes, which reconvey the condensed water to the boiler. The boiler may be constructed in the usual manner. The steam pipes are of cast-iron and placed vertically, or if horizontally, with a gentle slope towards the boiler. If several stories of a building have to be heated, a main steam-pipe is carried to the highest story, and branch pipes are fitted to it. The pipes are here and there fitted with air valves for the purpose of permitting the expulsion of the air compressed by the steam. The boiler, if low-pressure steam be used, should also be provided with an air valve, in order to prevent the collapse of the boiler by the outer atmospheric pressure if the generation of steam ceases. Heating by means of steam is advantageously applicable in works where steam is used as a motive power.

Combination of Steam and Hot-water Heating. Very recently it has been proposed to combine steam- with hot-water-heating, and to heat from one central locality a series of buildings and houses, in the same manner as these are now supplied from one central reservoir with gas or water.

Gas-Heating. It is well known that illuminating gas is now very generally used for the purpose of heating, being in this application best mixed with air, as is the case, for instance, in the Bunsen burner.

Gas is used for cooking in stoves specially constructed for the purpose, and also for heating apartments and buildings. As a rule it may be assumed that the combustion of 5 cubic feet of gas is sufficient to elevate the temperature of 1000 cubic feet of air 12°, and one-fifth of this quantity of gas suffices by its combustion to keep the temperature constant.

Heating without Ordinary Fuel. There is no doubt that an inexhaustible supply of heat exists as latent heat, which can be set free by friction, or, in other words, by the conversion of mechanical force into heat.

Notwithstanding many mechanicians have constructed apparatus for producing heat by mechanical force, none of these have been found practically available, and some were found to be extremely wasteful. The heat generated by the fermentation of manure is usefully applied to heating hothouses, by placing under the manure heap thin sheet-iron pipes, which convey the heat into the hothouse.

β. *Boiler Heating and Consumption of Smoke.*

Boiler Heating. Steam-boilers are as a rule built in brick-work, and in their construction, as well as that of the furnace they are fitted with, economy of fuel is the great object. The furnace is of course built with fire-bars and ash-pit. The grate or fire-bars consist of parallel cast-iron bars, the size and shape of which depend upon the kind of fuel to be used, while as regards the space between the bars experience has taught that the sum should not amount to more than one-fourth of the total surface of the grate. A large grate has the advantage of more freely admitting air to the fuel, while obstruction by clinker and slag is less to be feared. The operation of firing with a large grate is more easily conducted, and can take place at longer intervals of time. Of course the grate must be kept entirely covered with fuel. Small grates may be preferable in some instances, especially where a vivid combustion is required. Grates for wood fuel may have half the surface required for coal, as with the former the openings between the bars do not become choked with clinker and slag. According to E. Köchlin a grate for burning in one hour 350 kilos. of old oak wood should be of 1 square metre surface with ¼ square metre for space between the bars. Usually, however, the grates for wood fuel are made four times smaller than those for coal.

The fire-place or furnace should of course be constructed of sufficient height, width, and depth to admit of the proper combustion of the fuel. The fuel should be thrown into the furnace in sufficiently large quantity at once to keep up the steam adequately. Too frequent firing is not economical, because a large quantity of cold air is admitted, which cools the boiler and interferes with the proper combustion of the fuel. The dimensions of the furnace doors must bear a proper proportion to the size of the furnace, and these doors must close tightly so as to prevent draughts of air impinging on the burning fuel.

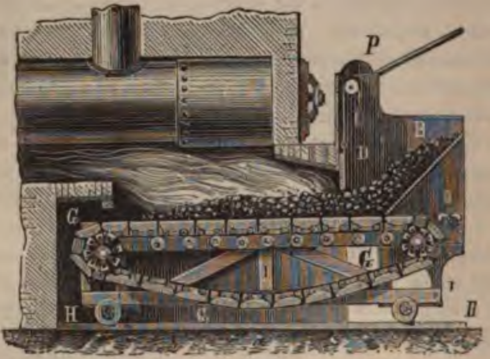
Smoke-Consuming Apparatus. While we cannot here enter into any further details on boiler-furnaces, a subject really belonging to engineering, we may now turn our attention to smoke-consuming furnaces, contrived with the view not only of abating the nuisance arising from the smoke evolved in huge volumes from large factory and other chimneys, but also for the saving of fuel, it having been ascertained that by the ordinary combustion of 1 ton of coals 25 lbs. of soot are evolved, having a heating power of four-fifths of the coal. The loss occasioned by the carbon thus carried off amounts to $\frac{1}{112}$th, or not quite 1 per cent.

When green coals are put in quantity on a bright boiler furnace, there is suddenly evolved an immense volume of combustible gases and vapours containing a large amount of carbon (benzol, toluol, carbolic acid, anthracen, naphthalin, paraffin, &c., the oxygen of the air contained in and supplied to the furnace being usually insufficient to cause the complete combustion of these substances, so that only the hydrogen burns, while the carbon is separated as smoke and soot, the evolution being promoted by the comparatively cool state of the boiler-plates, as well as by the large influx of cold air at the time of firing. The contrivances for preventing and consuming smoke are based upon different principles; for instance:—*a*. Air is sometimes conveyed to the fire-bridge by means of a separate pipe or channel. *b*. Two adjoining furnaces are connected and alternately fired in such a manner that the smoke of the furnace last fired is consumed in the high red heat of the other furnace. *c*. The fresh fuel is spread over only the front of the fire nearest the furnace-door, so that the evolved gases may be consumed by the red-hot fire on the bars. *d*. The feeding is effected by mechanical means, uninterruptedly, in such a manner that the fuel on the bars remains in a high state of incandescence. *e*. The construction of very high chimneys has been resorted to for the purpose of supplying a rapid current of air; but this expedient, a very expensive one, does not answer the purpose, and leads to loss of heat.

We may mention briefly the following smoke-preventing and consuming apparatus:—

1. Mechanical removal of the smoke by washing the products of combustion. In some chemical works near Newcastle-upon-Tyne the smoke of the different furnaces is washed by a spray of water previous to being passed into the chimney. For this purpose the smoke of the different furnaces of the work is conducted into subterranean brick-work channels, so constructed with knee-bends that the smoke is caused to flow upwards and downwards alternately, while at the mouth of the furnace-flue a continuous spray of water is caused to impinge upon the smoke, whereby all solid particles are thrown down and are removed from the channels as soot. There is in this case only one chimney, in which the draught is kept up by means either of a blast of air or a jet of injected steam. Jean, at Paris, has somewhat modified this method by causing the smoke and waste steam of a high-pressure engine to be conveyed into a subterranean channel covered with a layer of water several centimetres in depth, while a jet of cold water is made to play upon the smoke and steam. The channel is provided with a kind of water-wheel, which does not quite touch the surface of the water, but is fitted with brushes, which, touching the water, project it as spray through the channel. The water becomes heated, and serves after filtration as feed water.

Fig. 335.



2. Application of improved fire-bars, to be distinguished as (*a*) immovable, and (*b*) movable.

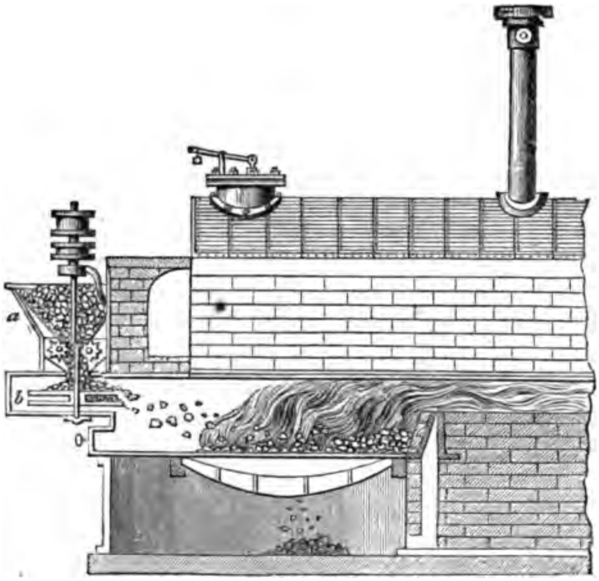
Step Grate. Among the immovable grates are the step- and stage-grates. The former consists of a series of step-like stages of fire-bars, to which the poker has access from the ash-pit. By the heat of the fire on the lower steps the fuel on the higher step is converted into coke, and only after this process has continued for some time is the partly-coked fuel raked down to a lower step, while fresh green coal is placed on the higher. The air enters this kind of grate not only through the space between the bars, but also laterally through the grated space between the steps. Caking-coal, or coal which makes much slag, does not answer as fuel in this grate, but small coal, refuse peat, sawdust, &c., are well adapted. Instead of iron fire-bars MM. Longridge and Mash make use of slabs of fire-clay, provided with channels and perforations so as to constitute a grating.

Etage or Stage Grate. This is a modification of the grate just described, and was invented by Langen (1866). The green fuel is not placed above the burning fuel, but under it, for which purpose the grate is constructed in stages, the fire-bars being inclined to the horizon at an angle of about 28°. There is between each *etage*, or stage, of the grate a space of about 12 centims. The fuel becomes coked, and the volatile products pass, mixed with air, through several stages of incandescent fuel, thus insuring complete combustion.

Movable Grates. The leading idea of these grates is to effect the firing by mechanical means. Among these the chain grate and rotating grate deserve notice.

Chain Grate. Notwithstanding the expensive nature of this invention, it has been found useful in practice and is employed in many establishments. It consists (Fig. 335) of two endless flat chains, G G, which run on two octo-geared rollers. Between these chains the fire-bars are placed longitudinally, so that the grate consists of an endless series of bars. The distance of the two rollers from each other determines the length of the grate. A rotating motion is imparted at O in such a manner that the grate moves through 27 to 30 millimetres per minute. The fresh fuel is thrown in at B, and is carried continuously towards the fire. The height of the layer of fuel is regulated by means of the slide-damper, D, which can be moved by means of the lever, *p*. The chains and rollers are supported by the truck, I, running on the iron rails, H H. The velocity of the grate is so regulated that the fuel is entirely consumed when arriving at the end of the fire-place. There are several serious defects in this apparatus. It is complicated, soon out of repair, requires a considerable amount of force to maintain its motion, and it does not altogether prevent smoke, while, finally, it is found wasteful for fuel.

FIG. 336.



Rotating Grate. This contrivance, invented by Collier, consists of a rotating disc which supplies the coal to the furnace uniformly through a slit cut below the furnace doors. This apparatus has never been extensively in use.

Improved Fuel Supply. 3. Among the numerous suggestions for the better feeding of furnaces are the following:—

Collier's feeder (1823) consists essentially of two horizontal crushing rollers provided with projections, so that the coal is broken up into uniform lumps, and then thrown into the fire by wheels provided with scoops revolving 200 times a minute. This mechanism requires a half nominal horse-power to maintain its motion.

Stanley's feeder, Fig. 336, consists of a funnel, *a*, fitted with toothed crushing rollers. The crushed coals fall on the distributor, *b*, which rotating with great velocity throws the coals uniformly on to the fire. Notwithstanding the defects of this invention, the chief being that it is not possible for the stoker to fire hard if required, this apparatus certainly prevents smoke, but is also liable to be quickly out of repair.

Pult Fires. Pult fires were first introduced by Wedgwood for porcelain furnaces. The characteristic feature is the mode of admitting air, which instead of entering as usual from below is forced downwards. The grate is placed in a sloping position. The fire-doors remain open, while the ash-pit is quite closed. This arrangement fulfils certainly all the conditions of complete combustion, but in practice has not answered and is only applicable with wood fuel.

Vogl's Grate. The fire-bars in this grate are placed at an angle of 33°. The coals are supplied by means of a funnel, and the bars can be shaken up and down by mechanical means.

Boquillon's Grate. An arrangement of rather complicated nature intended to be applied to house stoves, and so constructed that the green fuel is brought under the glowing fuel. The grate consists of a horizontal movable cylinder, upon which the fuel rests. When fresh fuel is added, this cylinder is turned so as to cause the fuel to be placed below the red-hot cinders. In practice this grate has not answered, being too complicated. **Apparatus of Cutler and George.** In many cases it has been attempted to feed the fires in an ascending mode, as, for instance, in Cutler's grate, improved upon by Arnott in 1854. The coals are burnt from an iron vessel which is by mechanical means lifted over the fire, the supply of coals in the vessel being regulated to last for twenty-four hours. In George's apparatus the fuel is supplied to the grate by means of a screw propeller.

Apparatus with Unequal Distribution. 4. Among the apparatus in which smoke is prevented by an unequal distribution of fuel on the grate, that of Duméry, deserves notice. This arrangement is distinguished from those of Cutler and George by the fresh fuel being put on from both sides of the grate under the red-hot cinders. For this purpose the grate is strongly curved upwards, exhibiting a saddle shape. The fuel is forced on to the grate by mechanical means in such a manner that it is first placed on the lowest fire-bars, and gradually forced towards the centre. This principle was known to Watt in 1785, and was applied by him in a slanting grate.

Tenbrinck also places the grate in a sloping direction, so that the coals tumble towards the fire-bridge, and accumulating there as incandescent coke cause the complete combustion of the fuel. In Corbin's grate a partition of fire-brick is employed. Fairbairn (1837) appears to have been the first to contrive smokeless grates. In his double grate the furnace is provided with two hearths, two grates, and two furnace doors. The grates are separated from each other by a partition of fire-bricks. The stoking is so regulated that while the one furnace is in full combustion, the other is supplied with fresh fuel, this operation occurring at regular intervals and alternately. The result is that the smoke and gases evolved are burnt by the highly incandescent fuel of the other furnace. De Buzonnière contrives to force the smoke of one furnace under the incandescent fuel of the other. With a properly regulated supply of air and regularity of stoking, it has been proved, by a series of experiments made on the large scale with a 40 horse-power marine multi-tubular boiler, by the late Dr. Richardson, of Newcastle-on-Tyne, and by Messrs. Longridge and Sir William Armstrong, that with all kinds of coal and with every variety of steam boiler, smokeless and complete combustion of the fuel may be obtained without difficulty, the plan being attended with a considerable saving of fuel and production of its highest calorific effect.

Consumption of Smoke by the Aid of Collateral Air Currents. 5. Nearly all attempts in this direction have proved an utter failure in practice. Parkes's (1820) split bridge was constructed with the view of causing the air to flow partly as usual under the grate, partly to act at the end of the furnace so as to effect a complete combustion. Palazot's invention, highly commended by Burnat, Tresca, and others, appears to be somewhat similar. Chanter's arrangement consists essentially of two grates placed parallel to each other. The green fuel is put upon one of these, and having been coked by the incandescence of the fuel on the other grate is raked on to that, thus insuring complete combustion increased by lateral jets of air.

Gall's Fire-place. Gall, reversing the rule that the dimensions of a factory chimney should bear a proportionate relation to the quantity of fuel to be burnt, has constructed chimneys, the highest point of which above the buildings is only 0·6 metre, and which, therefore, simply serve to carry off the products of combustion. As the difference of temperature is the cause of the draught of a furnace, Gall maintains a very high temperature in the combustion room; and in order to carry this out all the causes of loss of heat are reduced to a minimum in the following manner:—*a*. While in the ordinary mode of stoking the heat of the combustion room is necessarily lowered by the influx of cold air, the grating in Gall's arrangement is partitioned in such a manner that each compartment is gradually supplied with fresh fuel, by which arrangement the formation of smoke is prevented. *b*. The furnace is constructed so that the stoker cannot possibly put on too heavy a charge of green coals, while he is compelled to spread these uniformly over the fire. *c*. The loss of heat by radiation from the brick-work, fire-doors, &c., is prevented by causing the air required for the combustion of the fuel to pass these hot surfaces. *d*. Gall retards the velocity of the gases which escape to the chimney, while the surface of the grate and the section of the chimney are enlarged. Indeed, the entire arrangement is quite different from that in ordinary use, as the fire-bars are placed 3 metres below the boiler, while the grate is very deep. It was found, however, that when well built there was a sufficient draught, and steam could be kept up. Nothing is stated as regards the nature of the gases issuing from the chimney.

Resumé. As regards smoke consuming and preventing apparatus, it is only too evident that most of these do not answer the purpose so completely as might be expected. Practical experience has, however, taught that if the conditions of complete combustion are well attended to in the construction of the furnace, that with proper management and regular mode of stoking, adequate supply of air, and the application of the well-known means of preventing loss of heat by radiation, with coal, peat, or any other fuel, the combustion may be so conducted as to be smokeless; and at the same time the fuel thoroughly utilised.

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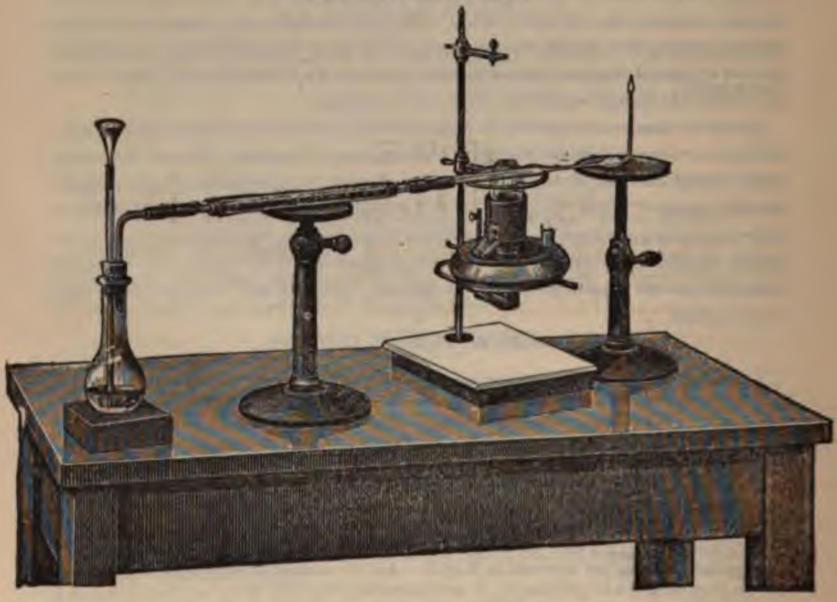

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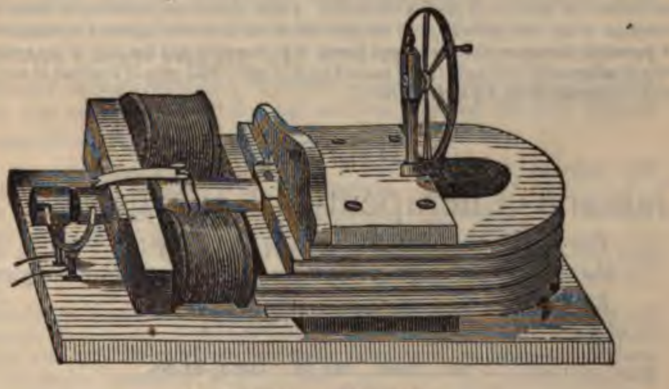

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